

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-286559

(43)Date of publication of application : 13.10.2000

(51)Int.Cl.

H05K 3/46

H05K 3/18

H05K 3/38

(21)Application number : 11-092415

(71)Applicant : HITACHI LTD

(22)Date of filing : 31.03.1999

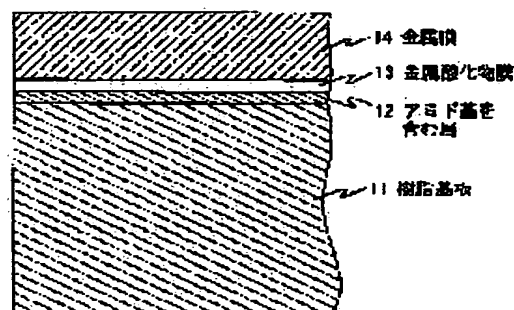
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(54) WIRING BOARD, PRODUCTION THEREOF AND SEMICONDUCTOR DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To form a micro wiring layer having high adhesion performance by specifying the line width and the thickness of the plating layer in a wiring layer formed on an insulating resin board through a modified layer and the mean roughness on the center line of the board at a part where the wiring layer is formed.

SOLUTION: A wiring layer of plating film having line width of 10-40 μm and thickness of 15-45 μm is formed on an insulating resin board 11 through a modified layer 12 formed on the surface thereof wherein the mean roughness at least on the center line of the board at a part formed the wiring layer is set at 1.0 μm . Consequently, a highly reliable wiring board excellent in adhesion between a conductive metal 14 and the resin board 11 and heat resistance can be obtained. Furthermore, a highly reliable multichip module excellent in heat resistance can be obtained by laminating a plurality of wiring boards, interconnecting respective layers, providing a connecting part with an IC on the uppermost surface and then mounting an IC.



LEGAL STATUS

[Date of request for examination]

20.07.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The center line average of roughness height of said substrate of the part by which the wiring layer which the Rhine width of face becomes from the plating film 10-40 micrometers and whose thickness are 15-45 micrometers through the deterioration layer formed in the front face of this resin substrate is formed, and this wiring layer is formed at least on the insulating resin substrate is 1.0 micrometers. Wiring substrate characterized by being the following.

[Claim 2] It is the wiring substrate which has a wiring layer on an insulating resin substrate, and is characterized by forming this wiring layer through each class containing the metal oxide layer formed in the deterioration layer containing the amide group formed in said resin substrate front face, and said wiring front face.

[Claim 3] It is the wiring substrate which has a wiring layer on an insulating resin substrate, and is characterized by forming this wiring layer through each class containing the metal oxide layer formed in the deterioration layer whose center line average of roughness height on said front face of a substrate formed in said resin substrate front face is 0.1-1.0 micrometers, and said wiring front face.

[Claim 4] Said wiring layer is a wiring substrate characterized by carrying out the laminating of a catalyst bed, the non-electrolyzed metal plating film, and the electroplating film to said metal oxide layer front face one by one in either of claims 1-3, and forming them in it.

[Claim 5] It is the wiring substrate characterized by said metal oxide layer consisting of an oxide of the metal which is ** rather than copper reduction potential in claim 2.

[Claim 6] The wiring substrate with which it is the insulating resin substrate with which an insulating resin substrate contains polyimide resin in claim 4, and the metal whose reduction potential is ** is characterized by being a metal containing at least one of nickel, tin, and cobalt rather than the reduction potential of said copper.

[Claim 7] The wiring substrate which the laminating of said insulating resin substrate and wiring layer is carried out by turns, and is characterized by having a bonding pad for semiconductor device connection on said resin substrate front face in either of claims 1-6.

[Claim 8] The wiring substrate which the laminating of the wiring substrate according to claim 1 to 6 is carried out on a ceramic wiring substrate, and is characterized by forming the bonding pad for semiconductor device connection in said insulating resin substrate front face.

[Claim 9] The semiconductor device characterized by the semiconductor device being connected to a bonding pad according to claim 7 or 8 by solder.

[Claim 10] In the manufacture approach of a wiring substrate of coming to prepare wiring which uses copper as a conductor on an insulating resin substrate The process which performs plasma treatment to said insulating resin substrate front face on which the dissolution rate to the mixed liquor of 30 degrees C of solution temperature which mixed a hydrazine hydrate and ethylenediamine at a rate of 7 to 3 consists of 1-micrometer resin which is the following by /. The process which prepares the metal layer of the metal whose reduction potential is ** with nonelectrolytic plating rather than copper reduction potential in the field as for which said resin substrate carried out plasma treatment, The manufacture approach of the wiring substrate characterized by including the oxidation process which forms the oxide layer of this metal in an interface with this metal layer that touches said resin substrate, and the process which forms a copper layer with nonelectrolytic plating on said metal layer.

[Claim 11] The manufacture approach of the wiring substrate characterized by including the process which forms the process and plating resist which give a plating catalyst in the field which performed plasma treatment of this resin substrate in claim 10 between the process which performs said plasma treatment, and the process which prepares a metal layer in the field as for which said resin substrate carried out plasma treatment.

[Claim 12] In the manufacture approach of a wiring substrate that wiring which uses copper as a conductor is prepared on the resin substrate

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a new wiring substrate and the semiconductor device which used it for the manufacture approach list.

[0002]

[Description of the Prior Art] In recent years, in connection with improvement in the speed of LSI technology, and densification, thinning of electronic-circuitry wiring, multilayering, and the further improvement in an electrical property are required, and manufacturing the multilayer-interconnection substrate which used for the substrate the organic insulating material which was excellent in surface smoothness, thermal resistance, dimensional stability, or dielectric characteristics to this demand is examined.

[0003] When forming wiring which consists of copper on an organic insulation resin substrate, it is the adhesion of copper wiring and a resin substrate which becomes a problem most. It was a stock-in-trade to raise conventionally adhesion with the metal membrane which it is [metal membrane] software etching or split-face-izing a resin substrate front face by putting in a rubber component into the resin of a substrate beforehand, and melting it with a solvent etc., and deposited the resin substrate front face on the resin substrate front face according to an anchor effect or the mechanical tangle effectiveness. About a detail, it is KLMittal. Edit It is collected into PolymerSurface Modification:Relevance to Adhesion (VSP publication, 1996). However, in order to acquire adhesion force sufficient by this approach, the irregularity of about dozens of microns was required, and it was difficult to make detailed wiring with Rhine width of face of dozens of microns or less. Then, development of adhesion promotion processing in which bring about high adhesion only by building irregularity sufficiently smaller than wiring / tooth-space width of face on a front face, and the adhesion does not deteriorate under an elevated temperature was desired.

[0004] as the approach of forming copper wiring on an organic insulation resin substrate — subTORAKUTO — law and an additive process are known. The subTORAKUTO method is the approach of removing the copper of a part unnecessary as wiring by etching, and producing a wiring circuit, after carrying out metallizing of the copper all over a substrate first. Generally as an approach of carrying out metallizing of the copper, CVD and a spatter are used for the whole surface. Moreover, the approach of attaching copper thinly all over a substrate by ** attachment radio solution copper plating, thickness-attaching copper with electrolytic copper plating after that, and carrying out is also proposed, for example, it is 0.3 micrometers by nonelectrolytic plating about copper to the whole surface of polyimide resin in JP,4-187778,A. Forge-fire attachment and the approach of thickness-attaching about 35 micrometers and carrying out with electrolytic copper plating, after that, are indicated. Since the configuration where had to etch the copper plate with the thickness of 10 micrometers or more on a resin substrate by the subTORAKUTO method, and it was not avoided that the lateral portion of copper wiring Rhine is also etched, but the side near the substrate of wiring Rhine became thin would be taken, it was difficult to build the thin Rhine tooth-space pattern, and the limitation built the Rhine tooth-space pattern which is about about 40 micrometers.

[0005] on the other hand — an additive process — a substrate top — a resist — a circuit pattern — building — it — meeting — a conductor — it is the approach of depositing a metal. By this approach, since the aspect ratio of copper wiring Rhine becomes the resolution and the EQC of a resist mostly, it is suitable for manufacture of detailed wiring. There are a semi additive method and a full additive method in this additive process.

[0006] back plating resist to which the semi additive method deposited the metal thinly on the substrate surface whole surface — creating — after that — a conductor — it is the approach of building wiring with thickness-attaching copper in the case of a metal many, it carrying out it with electroplating or nonelectrolytic plating, and carrying out dirty out of the substrate metal thin film after exfoliation for a resist. The approach of attaching copper to the copper-clad laminate which carried out dirty out of the copper very thinly with nonelectrolytic plating generally, and thickness-attaching, carrying out with after [resist formation] electrolytic copper plating or non-electrolytic copper plating, and carrying out dirty out of the copper thin film after resist exfoliation is used. However, although this approach is applied to a substrate in which a front face has the irregularity which is dozens of microns like the copper-clad laminate which carried out dirty out of the copper, since good adhesion is not acquired by the smoother substrate, it is inapplicable to it. Metals other than copper are first attached to a substrate, and the approach of thickness-attaching the after copper and carrying out it is also proposed in order to acquire higher adhesion. for example, the method of forming a substrate metal layer in JP,10-65061,A by vacuum deposition or the dry type galvanizing method of sputtering, and electrolytic copper [non-] plating and performing electrolytic copper plating on an insulating film to it continuously on it is indicated, and if this approach is used, a wiring substrate can

be manufactured by the semi additive method — the purport publication is carried out. Detailed wiring near a resist dimension is formed by preparing a substrate metal layer on an insulating substrate, thickness-attaching copper, carrying out it by electroplating, after forming a resist on it, and carrying out dirty out of the substrate metal layer after resist exfoliation. However, when a substrate metal and copper are intermingled, generally it is very difficult to etch only a substrate metal. Furthermore, when dirty out of the substrate metal is carried out, it is in width of face differing and a clearance being slightly generated between an insulating substrate and a substrate metal layer in the copper wiring section and the substrate metal section under it. If it does so, in case the laminating of the wiring substrate will be carried out by insulating adhesion resin, the problem of remaining as a void, without fully filling up this clearance with adhesion resin will be produced.

[0007] after a full additive method gives a plating catalyst first to a substrate on the other hand — plating resist — preparing — a conductor — it is the approach of carrying out nonelectrolytic plating of a metal, for example, the copper, and exfoliating a resist if needed, or leaving as a permanent resist, and manufacturing a wiring substrate. Since there is no dirty out process of a substrate metal thin film, there are few routing counters, and since the configuration of wiring is decided by the configuration of a resist and it is advantageous to detailed wiring formation, its full additive method is more desirable. furthermore — the case where substrate metals other than copper are used — an etching process — there is nothing — a conductor — since the configuration of the section is decided by the resist configuration, it does not generate the problem that a clearance is generated between the insulating substrate seen by the semi-additive method, and a substrate metal layer, either. However, the problem that it was difficult for adhesion to improve non-electrolytic copper plating to a resin substrate had become big **** of a full additive method. Although the approach of split-face-izing a resin substrate was also proposed in order to realize firm adhesion, it was difficult to use a substrate with the irregularity of dozens of micrometers or more, when building the thin Rhine tooth-space pattern 40 micrometers or less. Therefore, development of the non-electrolytic copper plating approach of realizing the firm adhesion force in which it does not exfoliate in nonelectrolytic plating on the resin substrate front face which has sufficiently small irregularity compared with the width of face of the Rhine tooth-space pattern was called for. Etching processing of the polyimide resin substrate front face is carried out, radio solution copper plating after catalyst grant is made JP,4-72070,A, and it is indicated that the high adhesion force is acquired by subsequently heat-treating at the temperature of 120 degrees C or more. However, by the approach currently indicated in this official report, with non-electrolytic copper plating, copper was not able to be thickness-attached to 1 microns or more, and was not able to be made into them.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the wiring substrate which has the high detailed wiring layer of adhesion, its manufacture approach, and a semiconductor device.

[0009]

[Means for Solving the Problem] This invention minds the deterioration layer formed on the front face of this resin substrate on the insulating resin substrate. 15-35 micrometers and thickness preferably 10-40 micrometers 15-45 micrometers, [the Rhine width of face] The center line average of roughness height of said substrate of the part in which the wiring layer which consists of plating film which is 15-35 micrometers preferably is formed in, and this wiring layer is formed at least is in the wiring substrate characterized by being [1.0 micrometers or less] 0.05-0.3 micrometers preferably. This invention has a wiring layer on an insulating resin substrate, and this wiring layer is in the wiring substrate characterized by being formed through each class containing the metal oxide layer formed in the deterioration layer containing the amide group formed in said resin substrate front face, and said wiring front face.

[0010] the center line average of roughness height on said front face of a substrate where this invention has wiring on an insulating resin substrate, and this wiring layer was formed in said resin substrate front face — 0.1-1.0 micrometers — desirable — 0.3-0.7 micrometers it is — it is in the wiring substrate characterized by being formed through each class containing the metal oxide layer formed in the deterioration layer and said wiring front face.

[0011] As for said wiring layer, it is desirable that the laminating of a catalyst bed, the non-electrolyzed metal plating film, and the electroplating film is carried out to said metal oxide layer front face one by one, and they are formed in it.

[0012] Adhesion is made to form well detailed wiring which sets Rhine width of face to 40 micrometers or less, and, for that purpose, this invention is 1.0 micrometers about the center line average of roughness height of an insulating resin substrate front face. It considers as the following. Although high adhesion was not acquired by the former at such surface roughness, such detailed wiring can be constituted by processing like this invention. Furthermore, also in the Rhine tooth-space pattern, it is made to 40 micrometers or less, is 10 micrometers or more preferably, and is more preferably referred to as 20-35 micrometers. Such detailed wiring is the value which was acquired by considering as 300 or more N/m as Peel reinforcement, and carried out the multiplication of the Peel reinforcement (N/m) and the Rhine width of face (micrometer) especially preferably 10,000 or more 15,000 It is 20,000 more preferably above. It is above, and it is desirable to consider as what has the more high Peel reinforcement as Rhine width of face is made small. Moreover, it considers as the value which carried out the multiplication of the Rhine width of face and its thickness, and a wiring layer is 2 400-1200 micrometers. Carrying out is desirable and it is 2 500-800 micrometers more. It is desirable.

[0013] An amide group is made to generate because this invention carries out reforming processing of the resin substrate front face excellent in thermal resistance and dimensional stability. By depositing the metal whose reduction potential is ** from copper reduction potential on it, and depositing copper on this metal layer, after

forming the oxide layer of this metal in both interface It is that from which a wiring substrate with the very high reliance which heightened the adhesion force of a resin substrate and copper, and suppressed degradation at the time of the elevated temperature of the adhesion as much as possible is obtained. When forming detailed copper wiring which has Rhine width of face of dozens of microns or less especially on a resin substrate, copper wiring is formed on a resin substrate with a very effective full additive method.

[0014] Artificers found out that an interaction worked very strongly between an amide group and a metal oxide film, as a result of examining wholeheartedly what kind of chemical interaction heightens the adhesion force of a resin substrate and the metal to deposit.

[0015] As for this invention, it is desirable that wiring which consists of an insulating resin substrate, a metal membrane which deposited on this resin substrate, a layer containing the amide group formed in said resin substrate side front face of the contact interface of this metal membrane and said resin substrate, and metallic-oxide film formed in said metal membrane side front face of said contact interface, and uses said metal membrane as a conductor is prepared on said resin substrate.

[0016] Moreover, as for this invention, in the wiring substrate which comes to prepare wiring which uses copper as a conductor on an insulating resin substrate, it is desirable to take the structure which carried out the laminating of the metal oxide layer of the metal whose reduction potential is **, the metal layer of this metal, and the copper layer one by one rather than the deterioration layer formed by performing plasma treatment in this insulating resin substrate front face on said insulating resin substrate and copper reduction potential.

[0017] Moreover, as for this invention, it is more desirable than copper reduction potential that the metals whose reduction potential is ** are nickel, tin, and a metal containing at least one of cobalt.

[0018] The dissolution rate to the mixed liquor which mixed a hydrazine hydrate and ethylenediamine at a rate of 7 to 3 in the manufacture approach of a wiring substrate that this invention comes to prepare wiring with which copper is used as a conductor on an insulating resin substrate is the basis of 30 degrees C of solution temperature. The process which performs plasma treatment to the resin substrate front face which consists of 1-micrometer resin which is the following by /, The process which prepares the metal layer of the metal whose reduction potential is ** with nonelectrolytic plating rather than copper reduction potential in the field as for which said resin substrate carried out plasma treatment, It is characterized by including the process which forms the oxide layer of this metal in an interface with this metal layer that touches said resin substrate, and the process which forms a copper layer with nonelectrolytic plating on said metal layer.

[0019] Moreover, in case this invention performs plasma treatment to an insulating resin substrate, it is desirable to have performed plasma treatment so that oxygen or nitrogen might be used as reactant gas and the center line average of roughness height on the front face of processing might be set to 0.1 micrometers or more and 1.0 micrometers or less.

[0020] Moreover, as for this invention, it is desirable to include the process which gives a plating catalyst to the field which performed plasma treatment of this resin substrate between the process which performs plasma treatment to a resin substrate, and the process which prepares a metal layer in the field as for which said resin substrate carried out plasma treatment, and the process which forms plating resist.

[0021] Moreover, the wiring substrate of this invention comes to carry out two or more layer laminating of the wiring resin layer which prepared wiring which consists of a metallic conductor on the insulating resin layer. In the wiring substrate which has opening on a front face and has a bonding pad for connecting with IC electrically within this opening The dissolution rate to the mixed liquor which mixed a hydrazine hydrate and ethylenediamine at a rate of 7 to 3 by the basis of 30 degrees C of solution temperature It is characterized by having the conductor which consists of a configuration which carried out the laminating of the resin layer which consists of 1-micrometer resin which is the following by /, the first metal layer containing at least one of nickel, tin, and cobalt, and the different second metal layer from the metal contained in this first metal layer one by one.

[0022] Moreover, this invention carries out the laminating of the ceramic wiring board which uses a ceramic as the component of an insulating layer, and the resin wiring substrate which uses resin as the component of an insulating layer, and sets it to a wiring substrate with the configuration which connected both electrically. The dissolution rate to the mixed liquor with which said resin wiring substrate mixed a hydrazine hydrate and ethylenediamine at a rate of 7 to 3 by the basis of 30 degrees C of solution temperature It is characterized by having the conductor which consists of a configuration which carried out the laminating of the insulating layer which consists of 1-micrometer resin which is the following by /, the first metal layer containing at least one of nickel, tin, and cobalt, and the different second metal layer from the metal contained in this first metal layer one by one.

[0023] Moreover, the dissolution rate to the mixed liquor with which this invention mixed a hydrazine hydrate and ethylenediamine at a rate of 7 to 3 in the manufacture approach of a wiring substrate that wiring with which copper is used as a conductor is prepared on the resin substrate is the basis of 30 degrees C of solution temperature. The layer which performs hydrophilization processing in the water solution which includes the resin substrate front face which consists of 1-micrometer resin which is the following by /for an alkali-metal hydroxide, and contains an amide group is formed. Next, the metal membrane whose reduction potential is ** is deposited rather than copper reduction potential on the layer containing said amide group. Next, it is characterized by making a metal oxide film form in said metal membrane front face of a contact interface with the layer containing said metal membrane and said amide group, performing non-electrolytic copper plating on said metal membrane after that, and depositing copper.

[0024] Drawing 1 is the cross-section block diagram of the wiring substrate of this invention. In making the metal on

a resin substrate into one kind, there is a deterioration layer formed by performing the layer or plasma treatment containing an amide group to the resin substrate side of the interface of a resin substrate and a metal layer, and there is a metal oxide layer in a metal layer side. Moreover, when making the metal on a resin substrate into one or more kinds, the second metal layer is formed on this metal layer. When the second metal is copper and it forms copper with nonelectrolytic plating especially, the first metal is a metal whose reduction potential is ** from copper reduction potential.

[0025] As a heat-resistant high insulating resin substrate concerning this invention, polyamide resin, polyimide resin, the poly benzo oxazole, polyamide imide resin, polybenzimidazole resin, aramid resin, an epoxy resin, etc. are mentioned. When non-electrolytic copper plating performs thickness attachment especially, that to which the dissolution rate to the mixed liquor which mixed a hydrazine hydrate and ethylenediamine at a rate of 7 to 3 fills with the basis of 30 degrees C of solution temperature the conditions of being the following by 1-micrometer/is desirable.

[0026] As heat-resistant high resin, polyamide resin, polyamide imide resin, etc. are mentioned including an amide group into a frame. Moreover, the polyimide which is made to carry out dehydration condensation of an acid anhydride and the amine, and builds them as heat resistant resin which can introduce an amide group into a front face, the poly benzo oxazole which heats a polyamide, is made to dehydrate and is built can be mentioned by carrying out surface treatment with a chemical. To the case of resin without the functional group which turns into an amide group, for example, polyethylene, an epoxy resin, etc., first, a carboxyl group can be introduced into a front face by strong acid processing, and an amide group can be generated by making it react with an amine. When the adhesion force with the metal attached on [after performing surface treatment processing which generates an amide group, or after performing plasma treatment] it was evaluated, polyimide resin showed the high adhesion force especially. Especially as a resin substrate from this, polyimide resin is desirable.

[0027] Generally, in the case of plasma treatment, it depends for the shape of surface type on the class of reactant gas used. However, for adhesion, also in the case of nitrogen [when the reactant gas to be used is oxygen], the center line average of roughness height of a deterioration layer front face is 0.1 micrometers. When it was above, it was high, and the adhesion reinforcement which can bear the practical use process of 500 or more N/m of 25-degree C bases was obtained as Peel reinforcement in 90 raising peel tests. The center line average of roughness height of the deterioration layer front face containing the amide group in which oxygen and nitrogen are desirable and are formed as reactant gas from this is 0.1 micrometers. It is desirable from the point of adhesion that plasma treatment is carried out so that it may become above. On the other hand, the center line average of roughness height is 1.0 micrometers. If a resin substrate front face is split-face-ized so that it becomes above, it will become impossible to disregard the irregularity of wiring and 15-30 micrometers of problems that the deterioration layer itself becomes weak will be produced, when building especially preferably 10-40 micrometers of detailed wiring of about 20 micrometers as Rhine/a tooth space. Therefore, the center line average of roughness height has 0.15-0.35 micrometers more desirable than 0.1 micrometers or more and 1.0 micrometers or less.

[0028] Reduction potential can mention nickel, cobalt, titanium, and chromium rather than copper reduction potential as a metal which is **. As the deposit approach of a metal layer and copper, although a spatter can also be used, in order to produce a circuit pattern using the fully-additive process suitable for detailed wiring formation, it is desirable to use nonelectrolytic plating. After the oxide layer of said metal deposits said metal thinly on a resin substrate beforehand, it is formed by performing oxidation treatment. Or after depositing said metal only in one field of a resin substrate, a metal oxide layer can be formed by supplying oxygen to an oxygen ambient atmosphere through a resin substrate at an interface by Lycium chinense. In order to cause the interaction of the resin substrate front face and metal oxide layer which carried out amide group generation processing, it is not [that both have just touched] related to especially both thickness.

[0029] Although it can form by the spatter and the copper of the maximum upper layer can also be formed by electroplating, when building a wiring substrate with a fully-additive process, forming with nonelectrolytic plating is desirable.

[0030] The so-called subTORAKUTO method which uses the suitable resist and builds a circuit pattern by etching to it after depositing a metal all over a resin substrate in production of a circuit pattern, The so-called semiadditive process which carries out dirty out of the ** attachment metal membrane of an unnecessary part after attaching a metal membrane thinly all over a resin substrate, stretching a resist and carrying out thickness attachment of the metal with electroplating or nonelectrolytic plating, since it crawls on a resist to a resin substrate — nonelectrolytic plating — a metal — thickness — attaching — carrying out — a conductor — the so-called fully-additive process which builds wiring can be used.

[0031] The following processes are also considered as a process which builds a wiring substrate with a fully-additive process. After giving the catalyst for plating all over the resin substrate which performed plasma treatment, a photosensitive dry film is laminated on a resin substrate front face, or coating desiccation of the photosensitive insulation resin coating liquid is carried out, and plating resist is formed in exposing and developing negatives. A postexposure and afterbaking are performed if needed. Then, reduction potential forms first the metal layer of the metal which is ** rather than copper reduction potential with nonelectrolytic plating. The oxide layer of this metal is formed in a resin substrate / this metal layer interface by performing this metal stratification afterbaking processing. Then, after dilute hydrochloric acid etc. removes the oxide film of this metal layer front face, it puts into a non-electrolytic copper plating bath, only desired thickness galvanizes copper, and a copper wiring substrate is completed.

[0032] as the approach of carrying out the laminating of the wiring layer — the coating liquid of insulating resin — a conductor — a wiring top — coating, and the process and conductor to dry — the approach of repeating successively the process which forms wiring is raised. Flattening of the insulating layer is ground and carried out if needed. moreover — the case where the film of insulating resin is used as an insulating layer — a resin film top — a conductor — wiring — forming — a conductor — a wiring sheet — making — a suitable binder sheet — inserting — another conductor — a wiring sheet can be piled up and a laminating can be carried out by heating and pressurizing. It is easily realizable of electric connection between each class with the beer hall formation which used the laser beam, the plating in a beer hall, or restoration of conductive paste.

[0033] For the purpose to be used, the wiring substrate of this invention can also be independently used as a flexible wiring substrate in itself, and can also be used as a wiring substrate with rigidity by preparing on a ceramic plate, a glass plate, a silicon wafer, etc. Moreover, the wiring substrate of this invention can be formed on a ceramic wiring board, and it can also use as a wiring substrate of one by taking both electric connection. Furthermore, since it can perform easily carrying two or more ICs in a front face, the wiring substrate of this invention can be used as a multi chip module substrate. It is suitable as a multi chip module substrate which mounts two or more ICs from the ability to form detailed copper wiring by the full additive method especially.

[0034] this invention persons found out that a specific functional group and a metaled oxide raised adhesion.

[0035] When polyimide was processed in the alkali water solution, the imide ring near the front face carried out ring breakage, and it confirmed that an amide group was made from total reflection infrared-absorption-spectrum measurement. as polyimide — the Du Pont make — the total reflection infrared absorption spectrum before and behind the processing at the time of using Kapton 200H is shown in drawing 2, and the differential spectrum is shown in drawing 3. Although a new absorption band has appeared in the 1650 or 1550cm⁻¹ neighborhood by surface treatment, it belongs to Amide I and an amide II absorption band, respectively. This spectrum change shows that the imide ring carried out ring breakage and the amide group is made. The catalyst for plating (HS[by Hitachi Chemical Co., Ltd.]-101B) was given to this front face, and copper plating was performed using non-electrolytic copper plating liquid (CUST[by Hitachi Chemical Co., Ltd.]- 2000). The temperature of plating liquid was 40 degrees and plating time amount was 3 seconds, and after drying enough by the vacuum drying after plating, it was left in day air. Change of said differential spectrum before and behind plating is shown in drawing 4. A clear change was looked at by Amide I and the amide II absorption band before and after plating. This change shows existence of the interaction of an amide group and the plating copper-plating film clearly.

[0036] Then, about about 30nm of copper films was attached to the polyimide which carried out surface treatment by the above-mentioned radio solution copper plating, with electrolytic copper plating, about about 20 micrometers of copper were thickness-attached, it was carried out, and the peel test estimated adhesion. Although there was almost no Peel reinforcement immediately after electrolytic copper plating, when it was left in air, adhesion improved remarkably with time amount. When it was left under an oxygen ambient atmosphere after carrying out an after [electrolytic copper plating] vacuum drying especially, the increment in the Peel reinforcement was remarkable. Aging of the Peel reinforcement is shown in drawing 5. It is shown that the adhesion of this result of both will improve remarkably clearly if a copper oxide film is made into the interface of polyimide and a plating copper film. Therefore, it turns out that a strong interaction works very much between an amide group and a copper oxide, and the adhesion force is discovered. Such a result was the same also about the case of the combination of metals other than polyimide and copper of other classes, for example, nickel, cobalt, titanium, etc. Moreover, it was not restricted only to polyimide resin and other resin, for example, poly benzo oxazole resin, and polybenzimidazole resin were also observed by this result. That is, when introducing the amide group into the resin front face by hydrolysis, it turned out that the same result is obtained.

[0037] Moreover, this invention persons made it clearer than a peel test that the strong interaction is working very much between metal oxide films like [the deterioration layer formed of plasma treatment] the layer containing the above-mentioned amide group, therefore that the very high adhesion force was acquired.

[0038] Furthermore, this invention persons perform the processing or plasma treatment which introduces an amide group into a resin ingredient front face. The adhesion of a resin ingredient and this metal layer improves by leaps and bounds by forming the oxide layer of this metal in an interface, after reduction potential forms the metal layer of the metal which is ** rather than copper reduction potential. Moreover, after adhesion built the high interface in this way, it found out that copper could be thickness-attached and could be carried out with nonelectrolytic plating on this metal layer.

[0039] Although the resin ingredient excellent in thermal resistance, dimensional stability, dielectric characteristics, etc. is suitable as a substrate ingredient which uses polyimide resin for a wiring substrate, especially an important point is that alkali resistance is high. Although the reaction for which reducing agents, such as formaldehyde, oxidize on a metal copper front face needs to occur in a non-electrolytic copper plating bath, in order for the reaction to cut, it must be alkalinity, therefore a wiring substrate ingredient will be put to alkaline liquid for a long time. When alkali resistance was low, the base material used as a foundation melted during non-electrolytic copper plating, and it was observed that the copper-plating film exfoliates. Then, the relation between alkali resistance and nothing-proof electrolytic copper plating bath nature was considered. As an alkali-proof index, the etch rate in the hydrazine hydrate / ethylenediamine (70/30, weight ratio) mixed liquor of 30 degrees C of solution temperature was used. The polyimide with which the macromolecule which has structures various in the combination of diamine and an acid anhydride as resin is obtained was chosen. Consequently, when the etch rate was the following by 1-micrometer/, it was confirmed that the plating film deposited on the substrate does not exfoliate even if it carries out plating for 15

hours or more in 70 degrees C of solution temperature and a with a pH of about 12 non-electrolytic copper plating bath. It turned out that this condition is not limited only to polyimide resin and other resin, for example, the poly benzo oxazole, polyamide resin, polyamide imide resin, polybenzimidazole resin, aramid resin, and an epoxy resin can also be applied.

[0040] Next, when galvanizing the above-mentioned resin substrate front face with non-electrolytic copper plating, how to acquire adhesion force sufficient between copper and a resin substrate was examined wholeheartedly. The substrate front face was reformed on condition that versatility, about 1 micrometer of copper was vapor-deposited by sputtering after that, after that, with electrolytic copper plating, it thickness-attached and thickness was carried out until it was set to 20 micrometers, and the Peel reinforcement was evaluated. Consequently, it became clear that the surface treatment approach of performing plasma treatment which makes reactant gas the method of processing a resin substrate front face with an alkali solution and oxygen, or nitrogen is effective. Especially, in the case of plasma treatment, it is 0.1 micrometers at the center line average of roughness height (Ra) to a resin substrate front face. The adhesion force in which adhesion with the especially high processing conditions which form the above irregularity is brought about, for example, the actual wiring substrate manufacture process of 500 or more N/m can be borne as Peel reinforcement in a 25-degree C basis and 90 raising peel tests came to be acquired.

[0041] When it galvanizes by giving the catalyst for plating to the resin substrate which performed the above-mentioned surface treatment processing, and putting into a non-electrolytic copper plating bath, it was not concerned with the value (10-13) of pH, and the temperature (20 to 80 degree C) of a plating bath, but the plating film has exfoliated in the phase of about 30nm or less of copper thickness. Also when non-electrolytic copper plating for thickness attachment was performed after performing flash plate radio solution copper plating for *****, the plating film for thickness attachment immediately after non-electrolytic copper plating initiation exfoliated, and thickness attachment was not completed. Therefore, it turned out that the adhesion force of the resin substrate front face and copper which performed reforming processing declines remarkably in a non-electrolytic copper plating bath. Then, after attaching metal membranes other than copper to the resin substrate front face, various things for which non-electrolytic copper plating is performed were examined. Consequently, after attaching metal membranes, such as nickel, tin, and cobalt, when non-electrolytic copper plating was performed, it found out that exfoliation of the plating film of a under [plating] would not take place. As a result of examining various metaled classes, it found out that it was more effective than copper reduction potential to attach beforehand the metal whose reduction potential is **. After attaching a metal membrane to a resin substrate at coincidence, it found out that the adhesion reinforcement of a resin substrate and a metal membrane improved it remarkably by making a metaled oxide film form between a resin substrate and a metal membrane by Lycium chinense at an oxidizing atmosphere. For example, the polyimide resin substrate front face was processed with the alkali solution, nickel was attached about 1 micrometer of thickness with nonelectrolytic plating on it, and when copper was thickness-attached about 20 micrometers of thickness, was carried out on nickel with electrolytic copper plating, the adhesion between polyimide/nickel was evaluated and the Peel reinforcement of the sample which carried out annealing treatment at 180 degrees C among atmospheric air after nickel plating for 2 hours, and the sample which is not processed was measured, the value of 900 N/m and 300 N/m was acquired respectively. It was observed also when the improvement in the adhesion by annealing after such plating performed plasma treatment as surface treatment of resin. This is considered because the oxide in an adhesion interface has the resin front face which has an amide group, the resin front face by which plasma treatment was carried out, and a chemical interaction.

[0042] From the above thing, the dissolution rate to the mixed liquor which mixed a hydrazine hydrate and ethylenediamine at a rate of 7 to 3 as a resin substrate by the basis of 30 degrees C of solution temperature Perform processing which introduces an amide group into a resin substrate front face using 1-micrometer resin substrate which is the following by /, or plasma treatment is performed. The metal layer of the metal whose reduction potential is ** is prepared in a processing side rather than copper reduction potential, and it finds out that thickness-attach a copper film and it is made with non-electrolytic copper plating on said metal layer by forming the oxide layer of this metal in an interface with this metal layer that touches said resin substrate, and came to complete this invention.

[0043] Furthermore, on the resin substrate which performed amide group installation processing or plasma treatment Plating resist is formed by the postexposure and development which laminated the dry film after giving a catalyst. By for example, the thing which it puts into a radio solution copper-plating bath, and copper is thickness-attached and is done for it after performing BEKU processing in atmospheric air, forming a nickel oxide film in a resin substrate / nickel interface after attaching nickel with nonelectrolytic plating, and removing a surface nickel oxide film It has the Rhine tooth-space pattern [be / it / about 20 micrometers] on a resin substrate, and came to find out the thing whose thickness is about 20 micrometers and for which detailed and copper wiring which is a high aspect ratio can be built.

[0044]

[Embodiment of the Invention] (Example 1) surface roughness — 0.1 micrometers the Du Pont make which is the following — it used for the resin substrate of the polyimide film which is Kapton 200H. The 10cmx10cm test piece was made and it processed for 2 minutes with the surface treatment treated water solution of 25 degrees C of solution temperature.

[0045]

[Surface treatment treated water solution presentation]

— Sodium hydroxide 100 g/l — ethylenediamine 70 g/l — ethanol The test piece which carried out 100 g/l processing

was stuck on the epoxy resin substrate containing glass fabrics, and the vacuum drying was performed also as that [25-degree C] for 3 hours. Then, when the front face of a test piece was pressed against germanium prism and total reflection infrared-absorption measurement was carried out, in addition to the absorption peak of the 1780cm⁻¹ and 1720cm⁻¹ neighborhood which belongs to the carbonyl group of an imide ring, the absorption peak peculiar to an amide group was observed by the 1650cm⁻¹ and 1550cm⁻¹ neighborhood. From this, it was checked that the amide group had been introduced into the front face by this surface treatment. Circuit PUREPPU 3040, 3340, and 4041 by Nippon Mining Co., Ltd. was used for this test piece, and catalyst processing for plating was performed to it by the predetermined approach. next, Hitachi Chemical — it galvanized using the non-electrolytic copper plating liquid for shrine CUST-2000 ** attachment. Thickness was about 30nm. The stream performed the vacuum drying also as that [25-degree C] after rinsing for 3 hours. Next, the sample was put on the bottom of an oxygen air current for 1 hour. The X-ray was irradiated on the low square from the resin substrate side of a sample, the diffraction spectrum was measured, the interface of a resin substrate and a copper film was investigated, and it confirmed that the copper acid ghost existed in the interface. Then, it is electrolytic copper plating the current density of 15mA/cm on a copper film 2 It carried out and thickness attachment was carried out about about 20 micrometers of thickness.

[0046]

[Electrolytic copper plating liquid presentation]

– Copper-sulfate 5 hydrate 0.80 mols/l. – sulfuric acid 0.54 mols/l. – sodium chloride 0.0014 mols/l. After electrolytic copper plating, after the stream washed enough, the vacuum drying was performed also as that [25-degree C] for 3 hours. The sample was stripped from the epoxy resin substrate containing glass fabrics, and the peel test which fixes a copper film side to a silicon wafer with a double-sided tape, and tears off a polyimide film side was performed. The exfoliation interface at the time of a peel test had exfoliated in the interface of polyimide and a copper film. The Peel reinforcement is 1.2 kN/m. The very high adhesion force was acquired. Moreover, the Peel reinforcement after leaving this substrate sample at 300 degrees C among nitrogen-gas-atmosphere mind for 1 hour was hardly changing with about 1.1 kN/m. Furthermore, after holding this substrate sample in 150-degree C atmospheric air for 1000 hours, when the peel test was performed, the Peel reinforcement was maintaining about 0.9 kN/m and very high adhesion reinforcement. This shows that it is very reliable in thermal stability, when this substrate is used as electronic parts.

[0047] (Example 2) as a polyimide film — the Du Pont make — Kapton 200H were used. The 10cmx10cm test piece was made and it processed for 2 minutes also as that of 25 degrees C of solution temperature with the same surface treatment treated water solution as what used this in the example 1. The test piece was stuck on the glass epoxy resin substrate after processing, and catalyst processing for plating was performed by the predetermined approach using circuit PUREPPU 3040, 3340, and 4041 by Nippon Mining Co., Ltd. next, non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1) — nickel — about 0.1 micrometers of thickness like — it attached. The sample was stripped from the glass epoxy resin substrate after plating, and after carrying out a vacuum drying for 3 hours, heating at 40 degrees C, it put on the bottom of an oxygen air current for 1 hour. The X-ray was irradiated on the low square from the polyimide film side of a sample, the diffraction spectrum was measured, the interface of a polyimide film and the nickel film was investigated, and it confirmed that the oxide of nickel existed in the interface. Then, thickness attachment of the copper was carried out about about 20 micrometers of thickness on the nickel film with electrolytic copper plating. The used electrolytic copper plating liquid and plating conditions are the same as an example 1. After electroplating, after carrying out a vacuum drying for 3 hours, heating a sample at 40 degrees C, it put on the bottom of an oxygen air current for 1 hour. Then, the peel test was performed by the same approach as an example 1. Consequently, the Peel reinforcement is about 1.6 kN/m. The very high adhesion force was shown. Moreover, the Peel reinforcement after leaving this substrate sample at 300 degrees C among nitrogen-gas-atmosphere mind for 1 hour is about 1.5 kN/m. It was hardly changing. Furthermore, after holding this substrate sample in 150-degree C atmospheric air for 1000 hours, when the peel test was performed, the Peel reinforcement is about 1.3 kN/m. Very high adhesion reinforcement was maintained. This shows that it is very reliable in thermal stability, when this substrate is used as electronic parts.

[0048] (Example 3) the Du Pont make of a polyimide film — Kapton 200H were used for the resin substrate. Four 5cmx5cm test pieces were made, and it processed for 2 minutes with the surface treatment treated water solution which indicated these in the example 1 of 25 degrees C of solution temperature.

[0049] The test piece was stuck on the epoxy resin substrate containing glass fabrics after processing, and the vacuum drying was performed also as that [25-degree C] for 3 hours. Then, the spatter of cobalt, tin, copper, and about about 1 micrometer of the nickel was respectively carried out to the test piece. Next, the sample was stripped from the epoxy resin substrate and it put on the bottom of an oxygen air current for 1 hour. The X-ray was irradiated on the low square from the polyimide film side of these samples, the diffraction spectrum was measured, the condition of the interface of a polyimide film and a metal membrane was investigated, and it confirmed that the oxide existed at the interface in any case of a metal sample. Then, thickness attachment of the copper was carried out about about 20 micrometers of thickness with electrolytic copper plating on the same conditions with the example 1 on each spatter metal membrane.

[0050] The vacuum drying was performed also as that [25-degree C] after electrolytic copper plating for 3 hours. The copper film was fixed to the silicon wafer with the double-sided tape, and the peel test which tears off a polyimide film side was performed. In any case of a sample, the exfoliation interface at the time of a peel test had exfoliated in the interface of polyimide and various metal membranes. As for the Peel reinforcement of each sample

of cobalt, tin, copper, and nickel, 1.5, 1.4, 1.2, 1.6 kN/m, and the very high adhesion force were acquired respectively. Moreover, the Peel reinforcement after leaving these substrate samples at 300 degrees C among nitrogen-gas-atmosphere mind for 1 hour was hardly changing respectively with 1.4, 1.4, 1.0, and 1.5 kN/m. Furthermore, after holding these substrate samples in 150-degree C atmospheric air for 1000 hours, when the peel test was performed, in any case, the Peel reinforcement was maintaining about 0.8 or more kN/m and very high adhesion reinforcement. This shows that it is very reliable in thermal stability, when these substrates are used as electronic parts.

[0051] (Example 4) 9.1 The 4 of the weight section and 4'-dihydroxy-m-benzidine was melted to the dimethylacetamide / pyridine mixed solvent of 50 weight sections (weight ratio 1:1), and the chlorination iso phthloyl of 10 weight sections was melted to the cyclohexanone of 50 weight sections. The latter solution was dropped at the former solution very slowly. The generated solid content was separated, this was dissolved in N-methyl pyrrolidone, the viscosity of this varnish was adjusted to about 50poise, pressure filtration was performed using the 10-micrometer membrane filter, and the minute insoluble element was removed. After applying this varnish to the glass plate with the spin coat method and heating it at 100 degrees C for 1 hour, it removed from the glass substrate and the film was obtained. The thickness of a film was 40 micrometers. Next, after fixing this film with an iron frame, carried out the continuation temperature up in 90 minutes from 100 degrees C to 400 degrees C under nitrogen-gas-atmosphere mind, and the dehydration condensation reaction was made to perform, and the poly benzo oxazole film was obtained. The 10cmx10cm test piece was made from this film, and it processed for 5 minutes 70 degrees C of solution temperature with the surface treatment treated water solution which indicated this in the example 1. After processing, trapezoid mold germanium prism was pushed against the test piece front face, and by the multiple echo ATR method, the surface infrared absorption spectrum was measured with the FT-IR measuring device (system 2000 by PerkinElmer, Inc.), and it confirmed that the amide group was generating on the front face. The test piece was stuck on the glass epoxy resin substrate, and catalyst processing for plating was performed by the same art with having indicated in the example 1. the next — an example 1 — the same — the Hitachi Chemical Co., Ltd. make —less — it galvanized for 2 minutes by the basis of 40 degrees C of solution temperature by electrolytic copper plating liquid CUST-2000. The thickness of the plating film was about 30nm. The sample was stripped from the glass epoxy resin substrate, and after carrying out a vacuum drying for 3 hours, heating at 40 degrees C, it put on the bottom of an oxygen air current for 1 hour. The X-ray was irradiated on the low square from the resin substrate side of a sample, the diffraction spectrum was measured, the condition of the interface of a resin substrate and a copper film was investigated, and it confirmed that the copper acid ghost existed in the interface. Then, thickness attachment of the copper was carried out about 20 micrometers of thickness with electrolytic copper plating. A presentation and plating conditions of the used electrolytic copper plating liquid are the same as an example 1. The resin film side was fixed to the silicon wafer with the double-sided tape, and the peel test which tears off a copper film was performed. Consequently, the Peel reinforcement is about 1.1 kN/m. The very high adhesion force was acquired. Moreover, the Peel reinforcement after leaving this substrate sample at 300 degrees C among nitrogen-gas-atmosphere mind for 1 hour was hardly changing with about 1.0 kN/m. Furthermore, after holding this substrate sample in 150-degree C atmospheric air for 1000 hours, when the peel test was performed, the Peel reinforcement was maintaining about 0.9 kN/m and very high adhesion reinforcement. This shows that it is very reliable in thermal stability, when this substrate is used as electronic parts.

[0052] (Example 5) Oxygen plasma treatment was performed for the epoxy group plate containing glass fabrics using the dry etching system (the product made from Anelva, DEA-506). Processing conditions are the pressure of 3Pa, and flow rate 25SCCM. The output of the plasma was set to 800W and processed for 45 minutes. Then, it rinsed, after processing for 5 minutes with the chromic-acid sulfuric-acid mixed water solution (the CrO35 section, sulfuric-acid 100 section, water 10 section) of 50 degrees C of solution temperature, and by ethylenediamine, immersion processing was carried out for 5 minutes, and it rinsed enough. Since the absorption peak identified by the amide group was observed by the 1650cm⁻¹ and 1550cm⁻¹ neighborhood when total reflection infrared-absorption measurement of the epoxy group plate front face after processing was carried out, it was checked that the amide group had been introduced into the front face by these processings. These three processing substrates were prepared, it let the mask with which Rhine/tooth space is formed at intervals of 5mm / 5mm on it pass, and titanium, chromium, and a tungsten thin film (about 50nm of thickness) were respectively formed by the spatter. Then, heat-treatment was performed for the sample at 180 degrees C for 2 hours, and the oxide film of various metals was formed in the interface of an epoxy resin substrate and various metal membranes. Attachment [the same conditions as an example 1 / with electrolytic copper plating / copper] on [various] the metal membrane 20 micrometers. Next, the peel test which tears off a copper film was performed. In any case of a sample, the exfoliation interface at the time of a peel test had exfoliated in the interface of an epoxy group plate and each metal membrane. As for the Peel reinforcement of each sample of titanium, chromium, and a tungsten, the adhesion force high in any case of 0.7, 0.6, 0.6 kN/m, and a metal was acquired respectively. Moreover, most Peel reinforcement after leaving these substrate samples at 300 degrees C among nitrogen-gas-atmosphere mind for 1 hour was not changing. Furthermore, after holding these substrate samples in 150-degree C atmospheric air for 1000 hours, when the peel test was performed, each Peel reinforcement is 0.5 kN/m. The above and comparatively high adhesion reinforcement were maintained. This shows that it is reliable in thermal stability, when these substrates are used as electronic parts.

[0053] (Example 1 of a comparison) the Du Pont make same as a polyimide film as an example 1 — the 10cmx10cm test piece was made using Kapton 200H, after sticking on a glass epoxy resin substrate, it rinsed with the stream enough, and even the plating catalyst grant process and the non-electrolytic copper plating process were performed

like the example 1. The thickness of the plating film was about 30nm. After plating, the sample was immediately stripped from the glass epoxy resin substrate, and thickness attachment of the copper was carried out with electrolytic copper plating on the same conditions as an example 1. Some copper-plating film began to exfoliate from the edge in about 10 minutes after plating initiation, and the whole plating film has exfoliated in about about 30 minutes.

[0054] (Example 2 of a comparison) the Du Pont make same as a polyimide film as an example 1 — the 10cmx10cm test piece was made using Kapton 200H, after sticking on a glass epoxy resin substrate, it rinsed with the stream enough, and even the surface treatment process, the plating catalyst grant process, and the non-electrolytic copper plating process were performed like the example 1. The thickness of the plating film was about 30nm. After plating, the sample was immediately stripped from the glass epoxy resin substrate, and thickness attachment of the copper was carried out about about 20 micrometers of thickness with electrolytic copper plating on the same conditions as an example 1. Some copper plating film exfoliated from the edge in electroplating. When the Peel reinforcement of the part which has not exfoliated after plating was measured like the example 1, only about 30 N/m extent and the very weak adhesion force were acquired. When a polyimide film and the copper-plating film were made to exfoliate all over the glove compartment filled up with nitrogen gas for the sample and the X diffraction of a copper-plating side front face was investigated, existence of a copper acid ghost was not accepted in an interface.

[0055] (Example 3 of a comparison) the Du Pont make same as a polyimide film as an example 1 — the 10cmx10cm test piece was made using Kapton 200H, after sticking on a glass epoxy resin substrate, the stream fully washed, and surface treatment performed catalyst processing for plating by the same art with having indicated in the example 1, without carrying out. Next, non-electrolytic copper plating was performed by the same approach with having indicated in the example 1, and copper was attached about about 30nm of thickness. The stream performed the vacuum drying also as that [25-degree C] after rinsing for 3 hours. Next, the sample was put on the bottom of an oxygen air current for 1 hour. When the X-ray was irradiated on the low square from the polyimide side of a sample, the diffraction spectrum was measured and the condition of the interface of a resin substrate and a copper film was investigated, it turned out that the copper acid ghost exists in the interface. Then, thickness attachment of the copper was carried out about about 20 micrometers of thickness with electrolytic copper plating on the copper thin film like the example 1. After electrolytic copper plating, after the stream washed enough, the vacuum drying was performed also as that [25-degree C] for 3 hours. The sample was stripped from the epoxy resin substrate containing glass fabrics, and the peel test which fixes a copper film side to a silicon wafer with a double-sided tape, and tears off a polyimide film side was performed. The exfoliation interface at the time of a peel test had exfoliated in the interface of polyimide and a copper film. The Peel reinforcement is 0.1 kN/m. Only the very low adhesion force was acquired.

[0056] In order to acquire the high adhesion force from the above thing by the interface of resin and a metal, in an existing [an amide group]-in resin front face, and metal side, it can be said that it is required for an interface part for an oxide film to exist.

[0057] (Example 6) as the resin substrate which consists of a polyimide film — the Ube Industries, Ltd. make — YUPI REXX 25S were used. Two 10cmx10cm test pieces were made, and oxygen plasma treatment was performed for these using the dry etching system (the product made from Anelva, DEA-506). Processing conditions are the pressure of 3Pa, and flow rate 25SCCM for output 800W, and processing-time 25 minutes. The processed test piece was stuck on the glass epoxy resin substrate, catalyst processing for plating was performed by the same art with having indicated in the example 1, and then nickel was attached about about 1 micrometer of thickness with non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1). Electrolytic copper plating was performed on the same plating conditions as an example 1 after that immediately, and thickness attachment of the copper was carried out about about 20 micrometers of thickness on the nickel film. Then, BEKU [one sample was paid into the vacuum dryer and / 180 degrees C] among the vacuum for 2 hours. BEKU [another sample / the same 180 degrees C] in atmospheric air for 2 hours. The side which the copper film of two samples attaches was fixed to the silicon wafer with the double-sided tape after BEKU, and the peel test which pulls up a 25-degree C basis and a polyimide film to the upper part 90 degrees, and tears them off was performed. Consequently, the Peel reinforcement of about 900 N/m was obtained and, as for what [BEKU / what / BEKU / what / in the vacuum / what / in about 300 N/m and atmospheric air], both were permitted the big difference. This shows that adhesion improves, if the oxide film of nickel is made into the interface of polyimide and the nickel film.

[0058] (Example 7) The poly benzo oxazole film was obtained by the approach indicated in the example 4. Three 5cmx5cm test pieces were made from this film, and plasma treatment was performed for this using the dry etching system (the product made from Anelva, DEA-506), using nitrogen as reactant gas. Processing conditions are the pressure of 3Pa, and flow rate 25CCM for output 800W, and processing-time 25 minutes. The test piece was stuck on the epoxy resin substrate containing glass fabrics after processing. Then, the spatter of titanium, cobalt, tin, and about about 1 micrometer of the nickel was respectively carried out to the test piece. Next, the sample was stripped from the epoxy resin substrate and it put on the bottom of an oxygen air current for 1 hour. The X-ray was irradiated on the low square from the poly benzo oxazole film side of these samples, the diffraction spectrum was measured, the condition of the interface of the poly benzo oxazole film and a metal membrane was investigated, and it confirmed that the oxide existed at the interface in any case of a metal sample. Then, thickness attachment of the copper was carried out about about 20 micrometers of thickness with electrolytic copper plating on the same conditions with the example 1 on each spatter metal membrane. The vacuum drying was performed also as that [25-degree C] after electrolytic copper plating for 3 hours. The copper film was fixed to the silicon wafer with the

double-sided tape, and the peel test which tears off the poly benzo oxazole film side was performed. In any case of a sample, the exfoliation interface at the time of a peel test had exfoliated in the interface of the poly benzo oxazole and various metal membranes. As for the Peel reinforcement of each sample of titanium, cobalt, tin, and nickel, 0.6, 0.8, 0.8, 1.0 kN/m, and the high adhesion force were acquired respectively. Moreover, most Peel reinforcement after leaving these substrate samples at 300 degrees C among nitrogen-gas-atmosphere mind for 1 hour was not changing. Furthermore, after holding this substrate sample in 150-degree C atmospheric air for 1000 hours, when the peel test was performed, in any case, the Peel reinforcement was maintaining 0.5 kN/m and high adhesion reinforcement. This shows that it is reliable in thermal stability, when these substrates are used as electronic parts.

[0059] (Example 8) The poly benzo oxazole film was obtained by the approach indicated in the example 4. The 10cmx10cm test piece was made from this film, and plasma treatment was performed for this using the dry etching system (the product made from Anelva, DEA-506), using an argon, oxygen, and nitrogen as reactant gas. Processing conditions are the pressure of 3Pa, and flow rate 25SCCM for output 800W, and processing-time 25 minutes.

[0060] The test piece was stuck on the epoxy resin substrate, and catalyst processing for plating was performed by the predetermined approach using circuit PUREPPU 3040, 3340, and 4041 by Nippon Mining Co., Ltd. Next, non-electrolyzed nickel plating (the TOPPUKEMI alloy B-1 by the Okuno Pharmaceuticals company is used) is performed, and it is 1.0 micrometers of thickness about nickel. It attached. The sample was stripped from the epoxy resin substrate, and after carrying out a vacuum drying for 3 hours, heating at 40 degrees C, it put on the bottom of an oxygen air current for 1 hour. When the X-ray was irradiated on the low square from the resin film side of a sample, the diffraction spectrum was measured and the condition of the interface of a resin film and the nickel film was investigated, it turned out that the nickel oxide exists in the interface. Then, thickness attachment of the copper was carried out about about 20 micrometers of thickness with electrolytic copper plating on the same conditions as an example 1. Next, the resin film side was fixed to the silicon wafer with the double-sided tape, and the peel test which tears off a copper film was performed. Consequently, the Peel reinforcement is 0.6, 0.9, and 1.0 kN/m, respectively, when reactant gas is an argon, oxygen, and nitrogen. The high adhesion force was acquired. Moreover, most Peel reinforcement after leaving these substrate samples at 300 degrees C among nitrogen-gas-atmosphere mind for 1 hour was not changing. Furthermore, after holding this substrate sample in 150-degree C atmospheric air for 1000 hours, when the peel test was performed, in any case, the Peel reinforcement is about 0.5 kN/m. High adhesion reinforcement was maintained. This shows that it is reliable in thermal stability, when these substrates are used as electronic parts.

[0061] (Example 9) as a resin substrate — the Ube Industries, Ltd. make — YUPI REXX 12.5S It used. Three 10cmx10cm test pieces were made from this film, and plasma treatment was respectively performed for these using the dry etching system (the product made from Anelva, DEA-506), using an argon, oxygen, and nitrogen as reactant gas. Processing conditions are the pressure of 3Pa, and flow rate 25SCCM for output 800W, and processing-time 25 minutes.

[0062] The test piece was stuck on the epoxy resin substrate, and catalyst processing for plating was performed by the predetermined approach using circuit PUREPPU 3040, 3340, and 4041 by Nippon Mining Co., Ltd. Next, non-electrolyzed nickel plating (the TOPPUKEMI alloy B-1 by the Okuno Pharmaceuticals company is used) is performed, and it is 1.0 micrometers of thickness about nickel. It attached. The sample was stripped from the epoxy resin substrate, and after carrying out a vacuum drying for 3 hours, heating at 40 degrees C, it put on the bottom of an oxygen air current for 1 hour. When the X-ray was irradiated on the low square from the resin substrate side of a sample, the diffraction spectrum was measured and the condition of the interface of a resin substrate and the nickel film was investigated, it turned out that the nickel oxide exists in the interface. Then, thickness attachment of the copper was carried out about about 20 micrometers of thickness with electrolytic copper plating on the same conditions as an example 1. Next, the copper film was fixed to the silicon wafer with the double-sided tape, and the peel test which tears off a resin film side was performed. Consequently, when reactant gas was an argon, oxygen, and nitrogen, as for the Peel reinforcement, 0.8, 1.0, 1.2 kN/m, and the high adhesion force were acquired, respectively. Moreover, most Peel reinforcement after leaving these substrate samples at 300 degrees C among nitrogen-gas-atmosphere mind for 1 hour was not changing. Furthermore, after holding this substrate sample in 150-degree C atmospheric air for 1000 hours, when the peel test was performed, in any case, the Peel reinforcement is about 0.6 kN/m. High adhesion reinforcement was maintained. This shows that it is reliable in thermal stability, when these substrates are used as electronic parts.

[0063] As an amine used as the raw material of polyimide, p-phenylene diamine (PDA), (Example 10) 4 and 4'-diamino diphenyl ether (DDE) is chosen. As an acid anhydride Pyromellitic acid 2 anhydride (PMDA), 3, 3', 4, and 4'-benzophenone tetracarboxylic dianhydride (BTDA), 3, 3', 4, and 4'-biphenyl tetracarboxylic dianhydride (BPDA) was chosen, both were melted to the equimolar [every] N-methyl pyrrolidone, it was made to react near a room temperature for about 5 hours, and the polyamic acid which is the precursor of polyimide was compounded. Then, pressure filtration was performed using the 10-micrometer membrane filter, and the minute insoluble element was removed. After applying this polyamic acid varnish with the spin coat method on the glass substrate and heating it at 100 degrees C for 1 hour, it removed from the glass substrate and the film was obtained. Next, after fixing this film with an iron frame, carried out the continuation temperature up in 90 minutes from 100 degrees C to 400 degrees C under nitrogen-gas-atmosphere mind, and the imide-ized reaction was made to perform, and the polyimide film was obtained. This film was made into the sample only in 10mm angle.

[0064] The etch rate measured and asked for thickness reduction of polyimide the test tube containing about ten cc of mixed liquor of a hydrazine hydrate / ethylenediamine (weight ratio 7:3) which adjusted this test piece at 30

degrees C by TARISU tetraethylpyrophosphate (product made from RANK TAILOR HOBSON) after predetermined time amount immersion. However, since polyimide was swollen by etching, thickness was measured after drying at 200 degrees C after rinsing. A result is shown in Table 1. The evaluation result of Kapton 200H (Du Pont-Toray make) of a polyimide film and Upilex-25S (Ube Industries, Ltd. make) marketed was also doubled and shown.

[0065]

[Table 1]

表 1

	ポリイミド		エッチング速度 ($\mu\text{m}/\text{分}$)	無電解めっき中の剥離 ○：剥離無し ×：剥離あり
	アミン	酸無水物		
合成 品	PDA	PMDA	10.3	×
	PDA	BTDA	0.3	○
	PDA	BPDA	0.04	○
	DDE	PMDA	1.5	×
	DDE	BTDA	0.06	○
	DDE	BPDA	0.03	○
市販 フィ ルム	Kapton 200H		10.1	×
	Upilex 25S		0.03	○

[0066] Moreover, the 10cmx10cm test piece was made and oxygen plasma treatment was performed for this using the dry etching system (the product made from Anelva, DEA-506). Processing conditions are the pressure of 3Pa, and flow rate 25SCCM for output 800W, and processing time 25 minutes. The test piece was stuck on the epoxy resin substrate containing glass fabrics after processing, and catalyst processing for plating was performed by the predetermined approach using circuit PUREPPU 3040, 3340, and 4041 by Nippon Mining Co., Ltd. Next, nickel was attached about about 1 micrometer of thickness with non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1). The sample was set under the oxygen air current after plating for about 1 hour. When the X-ray was irradiated on the low square from the resin substrate side of a sample, the diffraction spectrum was measured and the condition of the interface of a resin substrate and the nickel film was investigated, it turned out that the nickel oxide exists in the interface. The back, after attaching to a palladium-chloride water solution (1 g/l) about 1 minute, it put into the non-electrolytic copper plating bath for thickness attachment, and copper plating was performed. The presentation of the non-electrolytic copper plating liquid for thickness attachment is as follows. Solution temperature was held at 70 degrees C.

[0067]

[A non-electrolytic copper plating liquid presentation for thickness attachment]

– Copper-sulfate 5 hydrate 0.04 mols/l. – Disodium ethylenediaminetetraacetate 0.1 mols/l. – Formaldehyde 0.03 mols/l. – A sodium hydroxide 0.1 mols/l. – 2,2'-bipyridyl 0.0002 mols/l. – polyethylene glycol (average molecular weight 6000) It observed whether exfoliation of the plating film broke out during 0.03-mol [l.] plating. The result is shown in Table 1. Although exfoliation was not observed when a polyimide film with a slow etch rate was used for a substrate, in the case of the polyimide which is easy to be etched, exfoliation broke out between polyimide and the nickel film like plating initiation 30 minute. As for it, the result of Table 1 turns out that the alkali-proof strength of the polyimide of a substrate can show that the existence of exfoliation under non-electrolytic copper plating is influenced greatly, and an etch rate can prevent the exfoliation under non-electrolytic copper plating as it is the following by 1-micrometer/.

[0068] (Example 11) The polyimide film produced by the approach indicated in the example 10 was used as the 5cmx5cm angle, and was prepared every polyimide [each kind of] two sheets of every. After performing oxygen plasma treatment on condition that a publication of every one various kinds in the example 10, the test piece was stuck on the glass epoxy resin substrate, and copper was attached to the processing side about about 1 micrometer of thickness by sputtering. Copper was attached about about 1 micrometer of thickness by sputtering also about the unsettled film. All the samples were set under the oxygen air current for about 1 hour. When the X-ray was irradiated on the low square from the polyimide side of a sample, the diffraction spectrum was measured and the condition of the interface of polyimide and a copper film was investigated, it turned out that the copper acid ghost exists in the interface. When the X-ray was irradiated on the low square from the polyimide film side of these samples, the diffraction spectrum was measured and the condition of the interface of a polyimide film and a metal membrane was investigated, it turned out that the copper oxide exists at the interface in any case of a sample. Then, thickness attachment of the copper was carried out about about 20 micrometers of thickness with electrolytic copper plating about all samples. The presentation of the used electrolytic copper plating liquid is the same as an example 1. Current density was made into 0.015 A/cm². The copper film was fixed to the silicon wafer with the double-sided tape, and the peel test which pulls up the side which the copper of a 25-degree C basis and a polyimide film does not attach up, and tears it off at the include angle of 90 degrees was performed. The result is shown in Table 2. The evaluation result of Kapton 200H (Du Pont-Toray make) of a polyimide film and Upilex-25S

(Ube Industries, Ltd. make) marketed was also doubled and shown. In any case of polyimide, when oxygen plasma treatment was performed, compared with the case of being unsettled, the adhesion force improved remarkably.

[0069]

[Table 2]

表 2

	ポリイミド		ピール強度 (N/m)	
	アミン	酸無水物	未処理	酸素プラズマ処理
合成品	PDA	PMDA	50	600
	PDA	BTDA	100	900
	PDA	BPDA	50	600
	DDE	PMDA	150	1300
	DDE	BTDA	80	800
	DDE	BPDA	<30	700
	DDE	BPDA	<30	700
市販フィルム	Kapton 200H		50	600
	Upilex 25S		<30	700

[0070] (Example 12) It obtained by the approach which indicated the film of the polyimide which consists of combination of p-phenylene diamine (PDA), 3 and 3', 4, and 4'-biphenyl tetracarboxylic dianhydride (BPDA) in the example 10. The sample film was used as the 5cmx5cm angle, and was prepared four sheets. Oxygen plasma treatment was performed on the conditions which indicated this film in the example 10. Then, the test piece was stuck on the glass epoxy resin substrate, and catalyst processing for plating was performed by the same approach as what was indicated in the example 1. Non-electrolyzed nickel plating (B-TOPPUKEMI alloy by Okuno Pharmaceuticals company 1 use, about 1.0 micrometers of thickness), non-electrolyzed cobalt plating (De Dis clad by Okuno Pharmaceuticals company 601 use, about 0.8 micrometers of thickness), non-electrolyzed tinning (substar SN[by the Okuno Pharmaceuticals company]-2 use, about 0.7 micrometers of thickness), and non-electrolytic copper plating for ** attachment (CUST[by Hitachi Chemical Co., Ltd.]-2000 use, about 0.3 micrometers of thickness) were performed on these sample films, respectively. BEKU [the sample / with the electric furnace / that / 180-degree C] after plating for 2 hours. When the X-ray was irradiated on the low square from the polyimide film side of a sample, the diffraction spectrum was measured and the condition of the interface of polyimide and a metal membrane was investigated, it confirmed that the oxide of various metals existed in the interface. After it, the sample which carried out copper plating for ** attachment remained as it was, after attaching about 30 seconds at a palladium-chloride water solution (1 g/l) in the case of the sample which galvanized metals other than copper, was paid to the non-electrolytic copper plating bath for thickness attachment, and performed copper plating. The presentation of the non-electrolytic copper plating liquid for thickness attachment was the same as that of an example 10, and solution temperature was held at 70 degrees C. Exfoliation of the plating film was observed by the sample which carried out copper plating for ** attachment in about about 20 seconds after plating initiation. To it, by the sample which galvanized metals other than copper, even if about 3 hours passed, exfoliation was not observed. By the sample which carried out copper plating for *****, since the copper oxide film which is made of the interface with polyimide is returned during the non-electrolytic copper plating for thickness attachment, that in which exfoliation occurred is conjectured. Since the reduction reaction of an oxide does not occur and the interface of polyimide and a metal does not need to be destroyed if non-electrolytic copper plating for thickness attachment is performed after covering the resin substrate front face which performed surface treatment rather than copper reduction potential with the metal whose reduction potential is **, it is considered that exfoliation stops breaking out. Therefore, it can be said that it is indispensable to cover a resin substrate front face with the metal whose reduction potential is ** before performing non-electrolytic copper plating for thickness attachment.

[0071] (Example 13) as the resin substrate which consists of a polyimide film — the Ube Industries, Ltd. make — YUPI REXX 25S were used. The 10cmx10cm test piece was made and oxygen plasma treatment was performed for this using the dry etching system (the product made from Anelva, DEA-506). Processing conditions are the pressure of 3Pa, and flow rate 25SCCM. The output of the plasma changed by 200-800W, and the processing time was changed in 5 to 45 minutes. Moreover, plasma treatment was performed on the same processing conditions, using nitrogen as reactant gas. The processing side which performed these processings was observed with surface type voice analysis equipment (ESA[by Elionix, Inc.]- 3000), and it asked for the center line average of roughness height (Ra). Moreover, the processed test piece was stuck on the glass epoxy resin substrate, and catalyst processing for plating was performed by the same art with having indicated in the example 10. Next, nickel was attached about about 1 micrometer of thickness with non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1). BEKU [the sample / with the electric furnace in atmospheric air / that / 180-degree C] for 2 hours. When the X-ray was irradiated on the low square from the resin substrate side of a sample, the diffraction spectrum was measured and the condition of the interface of a resin substrate and the nickel film was investigated, it turned out that the nickel oxide exists in the interface. Then, it attached to the palladium-chloride water solution (1 g/l) about 30 seconds, and it put into the non-electrolytic copper plating bath for thickness attachment indicated in the

example 10 after that, copper plating was performed, and thickness attachment of the copper was carried out about about 20 micrometers of thickness. Solution temperature was held at 70 degrees C. Then, the side which the copper film attaches was fixed to the silicon wafer with the double-sided tape, and the peel test which pulls up a 25-degree C basis and a polyimide film to the upper part 90 degrees was performed. The result is shown in Table 3 with the measured value of the center line average of roughness height (Ra). The case of oxygen plasma treatment, and in the case of nitrogen plasma treatment, Ra is 0.1 micrometers. When it is above, it turns out that the high Peel reinforcement is obtained. On the other hand, plasma treatment time amount is long and Ra is 1.0 micrometers. If it becomes above, the Peel reinforcement will decrease conversely. Since the resinous principle had adhered to the exfoliative nickel film side when the exfoliation interface was observed, a polyimide front face becomes weak by plasma treatment, therefore it is thought that the Peel reinforcement decreased. Therefore, it is appropriate to carry out plasma treatment so that Ra may be set to 0.1 micrometers or more and 1.0 micrometers or less. By this, it is 0.5 kN/m. The wiring substrate of the copper in which the above high adhesion force is shown can be manufactured with non-electrolytic copper plating.

[0072]

[Table 3]

表 3

反応ガス	出力(W)	処理時間 (分)	R a (μ m)	ピール強度(N/m)
酸素	400	15	0.05	400
	800	5	0.07	500
	800	15	0.13	700
	800	25	0.19	900
	800	50	0.75	800
	800	75	1.32	300
窒素	400	15	0.06	400
	800	5	0.11	600
	800	15	0.15	1100
	800	25	0.21	1300
	800	50	0.53	1100
	800	75	1.05	400

[0073] (Example 14) as the resin substrate which consists of a polyimide film — the Ube Industries, Ltd. make — YUPI REXX 50S were used. Two 10cmx10cm test pieces were made, the dry etching system (the product made from Anelva, DEA-506) was used for these, and nitrogen plasma treatment was performed. Processing conditions are the pressure of 3Pa, and flow rate 25SCCM for output 800W, and processing-time 25 minutes. It was 0.2 micrometers when the center line average of roughness height on the front face of processing (Ra) was measured like the example 13. The test piece was stuck on the glass epoxy resin substrate after processing, and catalyst processing for plating was performed by the same art with having indicated in the example 10. Next, non-electrolyzed cobalt plating (De Dis clad by Okuno Pharmaceuticals company 601 use, about 0.8 micrometers of thickness) and non-electrolyzed tinning (substar SN[by the Okuno Pharmaceuticals company]-2 use, about 0.7 micrometers of thickness) were performed in each sample. BEKU [the sample / with the electric furnace in atmospheric air / that / 180-degree C] after plating for 2 hours. Then, it attached to the palladium-chloride water solution (1 g/l) about 30 seconds, and put into the non-electrolytic copper plating bath for thickness attachment indicated in the example 10 after that, and copper plating was performed. Solution temperature was held at 70 degrees C. Even if galvanized for about 10 hours, exfoliation was not observed but has galvanized copper about about 20 micrometers of thickness. When the peel test which pulls up a polyimide film to the upper part 90 degrees also as that [25-degree C], and is torn off after plating estimated the adhesion force with a copper film, in the case of the sample which galvanized cobalt and tin, the Peel reinforcement is about 900 and about 800Ns/m respectively, and has formed the thick film of the copper which had sufficient adhesion force with non-electrolytic copper plating on the polyimide film. Moreover, when the Peel reinforcement after setting these substrate samples under a 300-degree C elevated temperature by nitrogen-gas-atmosphere mind for 2 hours was measured, the Peel reinforcement showed the high Peel reinforcement equivalent to heat-treatment before, and adhesion did not fall by heat-treatment, either but it has manufactured the wiring substrate which has high dependability to thermal resistance.

[0074] (Example 15) as the resin substrate which consists of a polyimide film — the Ube Industries, Ltd. make — YUPI REXX 50S were used. The 10cmx10cm test piece was made and oxygen plasma treatment was performed on the conditions which stuck and fixed to the stainless plate and indicated this in the example 10. The catalyst for plating was given after processing by the approach indicated in the example 10. Next, the photosensitive negative-mold dry film was laminated, exposure development was carried out and plating resist was formed in the test piece front face. Rhine / tooth-space spacing of the minimum resist were 20 micrometers. The test piece was removed

from the stainless plate and nickel was attached about about 1 micrometer of thickness with non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1). After BEKU [a sample / with the electric furnace in atmospheric air / that / 180-degree C] for 2 hours, it attached to the palladium-chloride water solution (1 g/l) about 30 seconds, and put into the non-electrolytic copper plating bath for thickness attachment indicated in the example 10 after that, and copper plating was performed. Solution temperature was held at 70 degrees C. Even if galvanized for about 10 hours, a resist and a plating copper film did not occur but exfoliation has galvanized copper for them about about 20 micrometers of thickness. There is no exfoliation etc. between a copper wiring part and a polyimide substrate, and good adhesion was shown. When the copper wiring part was observed with the optical microscope and the scanning electron microscope, the copper circuit pattern which reproduced the configuration of a resist well was obtained. It was checked that a copper circuit pattern with a spacing [Rhine / tooth-space spacing] of 20 micrometers can be formed. When the cross section of the copper wiring section was observed, few level differences were not looked at by the interface of nickel and copper, either, but the configuration of the copper wiring section was faithfully reproduced as a replica of the configuration of a resist. Moreover, when the peel test which tears off wiring with a Rhine width of face of 5mm upwards 90 degrees was performed, the value with the Peel reinforcement very high in m and about 900Ns / was acquired. Furthermore, when the Peel reinforcement after setting this substrate sample under a 300-degree C elevated temperature by nitrogen-gas-atmosphere mind for 2 hours was measured, the Peel reinforcement showed the high Peel reinforcement equivalent to m, about 900-N [/], and heat-treatment before, and adhesion did not fall by heat-treatment, either but it has manufactured the wiring substrate which has high dependability to thermal resistance.

[0075] (Example 16) The poly benzo oxazole film was obtained by the approach indicated in the example 4. Thickness was 40 micrometers. This film was made into the sample only in 10mm angle. the place which measured the etch rate by the same approach as the approach indicated in the example 10 — an etch rate — a part for about 0.6-micrometer/ it was . Next, the 10cmx10cm test piece was made and oxygen plasma treatment was performed on the conditions which indicated this in the example 10. The test piece was stuck on the glass epoxy resin substrate after processing, and catalyst processing for plating was performed by the same art with having indicated in the example 10. Next, nickel was attached about about 1 micrometer of thickness with non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1). After BEKU [a sample / that / 180-degree C] among atmospheric air for 2 hours, it attached to the palladium-chloride water solution (1 g/l) about 30 seconds, and put into the non-electrolytic copper plating bath for thickness attachment indicated in the example 10, and copper plating was performed. Solution temperature was held at 70 degrees C. Even if galvanized for about 10 hours, exfoliation was not observed but has galvanized copper about about 20 micrometers of thickness. When the peel test which pulls up a 25-degree C basis and a copper film to the upper part 90 degrees, and tears them off after plating estimated the adhesion force with a copper film, the Peel reinforcement is about 700Ns/m, and sufficient adhesion was acquired. Moreover, when the Peel reinforcement after setting this sample under a 300-degree C elevated temperature by nitrogen-gas-atmosphere mind for 2 hours was measured, the Peel reinforcement showed the Peel reinforcement equivalent to about 650 N/m and heat-treatment before.

[0076] (Example 17) as the resin substrate which consists of a polyimide film — the Ube Industries, Ltd. make — YUPI REXX 50S were used. The 10cmx10cm test piece was made and it processed by the basis of 70 degrees C of solution temperature with the surface treatment treated water solution which indicated this in the example 1. The test piece was stuck on the epoxy resin substrate containing glass fabrics after processing, and catalyst processing for plating was performed by the same art with having indicated in the example 1. Next, nickel was attached about about 1 micrometer of thickness with non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1). BEKU [the sample / with the electric furnace in atmospheric air / that / 120-degree C] for 2 hours. Then, it attached to the palladium-chloride water solution (1 g/l) about 30 seconds, and put into the non-electrolytic copper plating bath for thickness attachment indicated in the example 10 after that, and copper plating was performed. Solution temperature was held at 70 degrees C. Even if galvanized for about 10 hours, exfoliation was not observed but has galvanized copper about about 20 micrometers of thickness. The copper film was fixed to the wafer after plating, and when the peel test which pulls up a polyimide film to the upper part 90 degrees, and tears it off estimated the adhesion force with a copper film, the Peel reinforcement is about 900Ns/m, and has formed the thick film of the copper which had sufficient adhesion force with non-electrolytic copper plating on the polyimide film. Therefore, the manufacture approach of a wiring substrate advantageous to low-cost-izing which is wet and can perform all processes can be offered.

[0077] (Example 18) a copper-clad laminate — using — subTORAKUTO — the conductor formed by law — the manufacture approach of the wiring substrate which carried out the laminating of the detailed wiring layer formed with the fully-additive process on the circuitry layer is explained. A manufacture process is shown in drawing 6 . the resin plate 22 which consists of polyimide — a copper 21 flare laminate — a photosensitive dry film (the Du Pont make, squirrel ton 1051) — laminating — a desired conductor — (a) which was made to carry out ultraviolet-rays exposure through the mask with which the circuit pattern was drawn, and was able to be burned in the image. subsequently, 1-1-1 trichloroethane — development — carrying out — a cupric-chloride etching reagent — using — un — a conductor — (b) which exfoliated the dry film with the methylene chloride after removing the copper of the section. this first pass — a conductor — after carrying out immersion coating of the toluene solution of 20mM (s) of triethoxysilane (3-aminopropyl) (Aldrich make) on a circuit, it dried at 110 degrees C for 30 minutes. The polyimide varnish (PIQ-L100 by Hitachi Chemical Co., Ltd.) was applied on it, the cure was carried out with the curing temperature of 400 degrees C, and the polyimide layer of about 15 micrometers of thickness was obtained.

Opening of the interlayer connection hole ($\phi 50$ micrometer) was carried out to the position of this polyimide layer front face with the excimer laser (KrF), and the residue was removed by DESUMIA processing (c). Subsequently, oxygen plasma treatment and catalyst grant were performed on the polyimide front face of a surface layer one by one on the conditions indicated in the example 10. Next, the resist 24 which becomes a polyimide front face from a photosensitive negative-mold dry film was laminated, negatives were exposed and developed through the mask, and plating resist was formed. When forming plating resist, the mask was produced and used so that the catching hole prepared at the last process and its land might be exposed. Rhine / tooth-space spacing of the minimum resist were 20 micrometers. Next, nickel 25 was attached about 1 micrometer of thickness with non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1). a substrate — the electric furnace in atmospheric air — a 180-degree C basis — the non-electrolytic copper plating bath for thickness attachment which attached to the palladium-chloride water solution (1 g/l) about 10 seconds after BEKU for 2 hours, and was indicated in the example 10 after that — putting in — copper plating — carrying out — the second layer on a polyimide layer — a conductor — formation of a circuit pattern, and the first pass — a conductor — a circuit and the second layer — a conductor — the connection in the catching hole which connects a circuit — a conductor — the section was formed. The temperature of a plating bath galvanized by having held at 70 degrees C for 8 hours, and formed the copper film of about 16 micrometers of thickness (d). Then, it was filled up with the catching hole with a copper paste. Next, the polyimide varnish was applied again, the polyimide layer was formed, exposure development of the catching hole was carried out after laminating an after [opening] photosensitivity dry film, the resist for plating was prepared, nonelectrolytic plating performed metallizing inside wiring layer formation and a catching hole like the above, and, finally the copper paste 26 was filled up with laser in the catching hole (e). The perspective view of the produced wiring substrate is shown in drawing 7. When the copper wiring part of the maximum upper layer was observed with the optical microscope and the scanning electron microscope, the copper circuit pattern which reproduced the configuration of a resist well is obtained, and it was checked that the copper circuit pattern with a Rhine width of face [of 30 micrometers], and a spacing [Rhine / tooth-space spacing] of 20 micrometers can be formed. Even if it left this substrate in 150-degree C atmospheric air for 1000 hours, exfoliation of an open circuit and wiring was not observed. Therefore, this wiring substrate has the high dependability over the actuation under the elevated temperature over a long period of time.

[0078] (Example 19) The manufacture approach of the wiring substrate which carried out the two-layer laminating of the detailed wiring layer formed with the fully-additive process on the silicon wafer substrate is explained. The mimetic diagram of a manufacture process is shown in drawing 8. After carrying out immersion coating of the toluene solution of 20mM(s) of triethoxysilane (3-aminopropyl) (Aldrich make) to a silicon wafer, it dried at 110 degrees C for 30 minutes. The polyimide varnish (PIQ-L100 by Hitachi Chemical Co., Ltd.) was applied on it, the cure was carried out with the curing temperature of 400 degrees C, and the polyimide film 32 was obtained (a). Thickness was 5 micrometers. Oxygen plasma treatment and catalyst grant were performed on this polyimide film front face on the conditions indicated in the example 5. Next, the photosensitive negative-mold dry film was laminated, exposure development was carried out and plating resist was formed in the sample front face. Rhine / tooth-space spacing of the minimum resist were 20 micrometers. next, non-electrolyzed nickel-plating liquid (the Okuno Pharmaceuticals company make B-1) — nickel 34 — about 0.4 micrometers of thickness like — it attached. After BEKU [a sample / with the electric furnace in atmospheric air / that / 180-degree C] for 2 hours, it attached to the palladium-chloride water solution (0.2 g/l) about 10 seconds, and put into the non-electrolytic copper plating bath for thickness attachment indicated in the example 10 after that, and copper plating was performed. Solution temperature was held at 70 degrees C. It is plating 2.5 Even if it performed time amount, a resist and a plating copper film did not occur but exfoliation has galvanized the copper film 33 for them about about 5 micrometers of thickness. Then, plating resist was exfoliated (b). There is no exfoliation etc. between a copper wiring part and a polyimide film, and good adhesion was shown. Furthermore, on this first wiring layer, hot press of the polyimide film (YUPI REXX 12.5 by Ube Industries, Ltd. S) was carried out through the adhesive film 36 (the Hitachi Chemical Co., Ltd. make N4, adhesion temperature of 250 degrees C, 10 micrometers of thickness), it pasted up, and the second insulating layer was formed (c). Opening of the interlayer connection hole ($\phi 50$ micrometer) was carried out to the position of this second insulating-layer front face with the excimer laser (KrF), and the residue was removed by DESUMIA processing (d). subsequently, the thing for which the same process as the case where the first wiring layer is formed using plating resist 37 is repeated — the second layer on the second insulating layer — a conductor — formation of a circuit pattern, and the first pass — a conductor — a circuit and the second layer — a conductor — the connection in the catching hole which connects a circuit — a conductor — (e) in which the section was formed. The place which ground the cross section and was observed with the optical microscope and the scanning electron microscope after cutting the produced substrate by the dicer, The copper circuit pattern which reproduced the configuration of a resist well is obtained, and the circuitry layer can form the copper wiring circuit pattern with a spacing [Rhine / tooth-space spacing] of 20 micrometers the second conductor with the circuitry layer the first conductor. It was checked that copper plating inside a hole was attached also in the interlayer connection hole, the surroundings are good and electrical installation can be taken certainly. Moreover, even if it leaves this substrate in 150-degree C atmospheric air for 1000 hours, exfoliation of an open circuit and wiring is not observed but this wiring substrate has the dependability high [exfoliation] over the actuation under the elevated temperature over a long period of time.

[0079] (Example 20) The manufacture approach of the multi chip module substrate formed by carrying out the laminating of the wiring substrate which prepared copper wiring with the fully-additive process on the insulating

resin substrate on the ceramic substrate manufactured according to the thick-film process of a conventional method is explained. Drawing 9 explains the example of the production process of this module. Copper wiring was formed only in one side of a polyimide film (YUPI REXX 12.5 by Ube Industries, Ltd. S) by the same approach as an example 18, and the one side wiring sheet 41 with a wiring layer was produced on one side. The parallel monotonous press was used for the sense to which a copper wiring layer side touches an adhesive film through an adhesive film 42 (the Hitachi Chemical Co., Ltd. make N4, adhesion temperature of 250 degrees C, 10 micrometers of thickness) in this wiring sheet on a ceramic substrate, and it pasted up. Then, it was filled [in order to take the electric connection between the pad section on a ceramic substrate 43, and a wiring layer,] up with the copper paste 44 after carrying out opening of the interlayer connection hole (phi50micrometer) to a position with an excimer laser (KrF, 248nm), removing a residue by DESUMIA processing, and carrying out metallizing of the inside of a catching hole about 5 micrometers of thickness by the selection copper-plating method (b).

[0080] Drawing 10 is the fragmentary sectional view of the multi chip module which formed the multilayer-interconnection resin substrate of six layers on the ceramic substrate obtained by drawing 9 , and carried the LSI chip by the flip-chip-bonding method.

[0081] On this wiring sheet, the wiring sheet in which copper wiring was formed was pasted up using the parallel monotonous press through the same adhesive film 42 as the above by the approach same to both sides of a polyimide film as an example 18. Next, the parallel monotonous press was used for the sense to which a copper wiring layer side touches an adhesive film through the same adhesive film 42 as the above in the one side wiring sheet 41 which formed and produced copper wiring by the same approach as an example 18 only on one side of a polyimide film (YUPI REXX 12.5 by Ube Industries, Ltd. S), and it pasted up. Opening of the predetermined part of the front face of the sheet which carried out the laminating was carried out with the excimer laser (KrF, 248nm), and the surface layer (Cr/nickel/Au) was formed. Then, plurality was carried for the LSI chip by flip chip bonding, and the multi chip module was produced. Even if this wiring substrate passed through the solder connection process, exfoliation of an open circuit and wiring was not observed but was understood that the dependability over an elevated-temperature process is high.

[0082]

[Effect of the Invention] according to this invention — a conductor — a wiring substrate with the high dependability which was excellent in the adhesion of a metal and a resin substrate, and was excellent in thermal resistance can be obtained. Consequently, it has desired thickness and detailed wiring of 40 micrometers or less is attained as Rhine width of face.

[0083] Moreover, by carrying out two or more laminatings of the above-mentioned wiring substrate, it can consider as a laminated circuit board, electric connection between each class can be made, and the reliable multi chip module excellent in thermal resistance can be obtained by preparing a connection with IC in the maximum front face, and carrying IC.

[Translation done.]

* NOTICES *

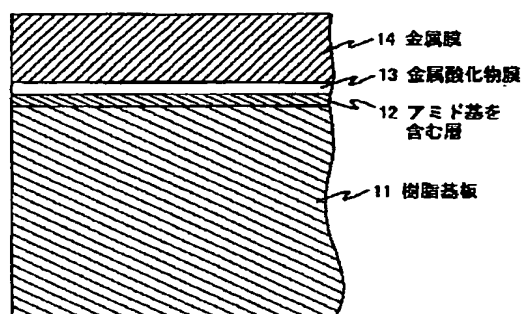
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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

図 1



[Drawing 2]

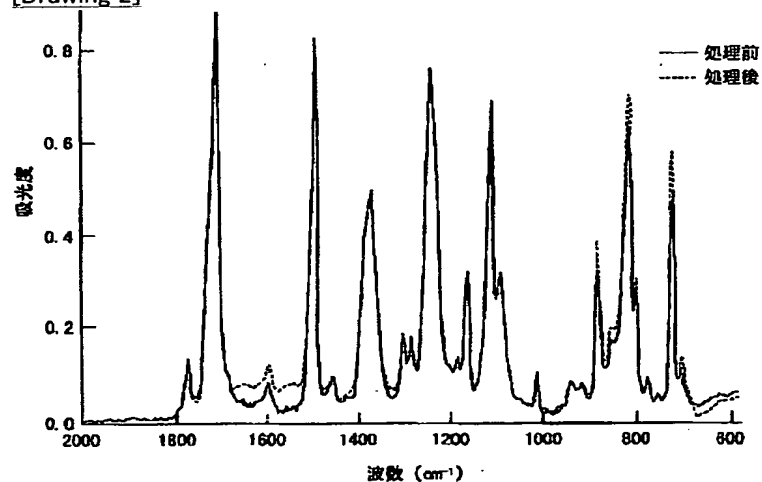


図 2

[Drawing 3]

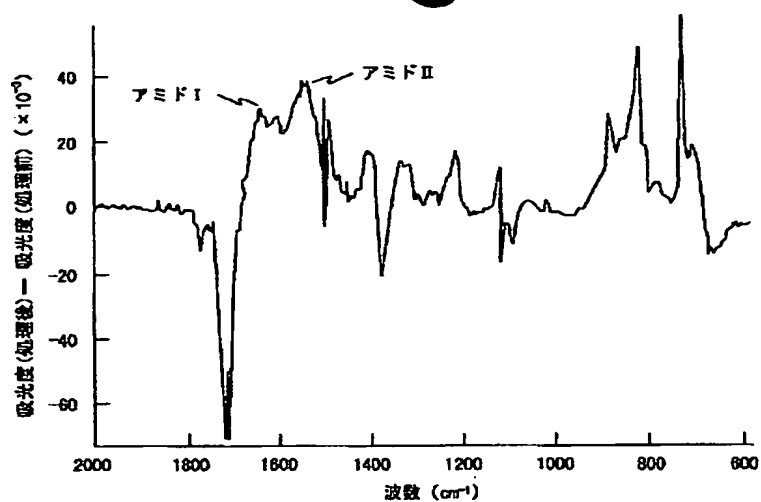
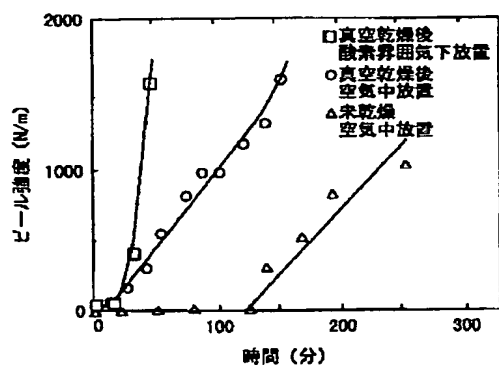


図 3

[Drawing 5]

図 5



[Drawing 4]

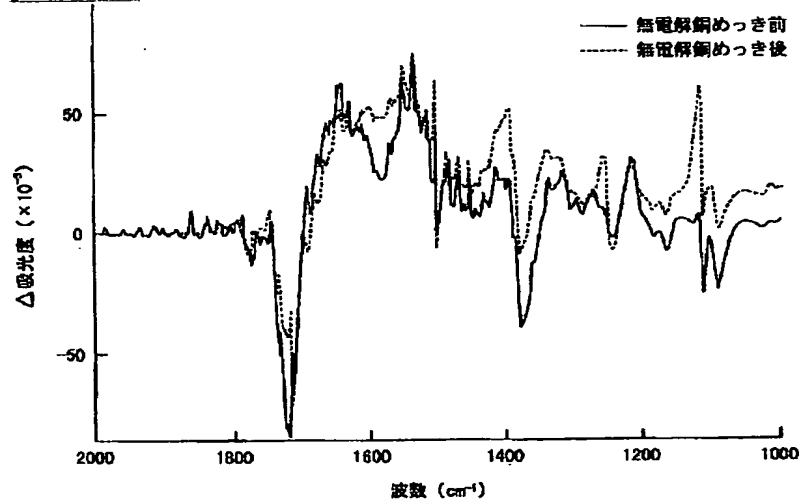
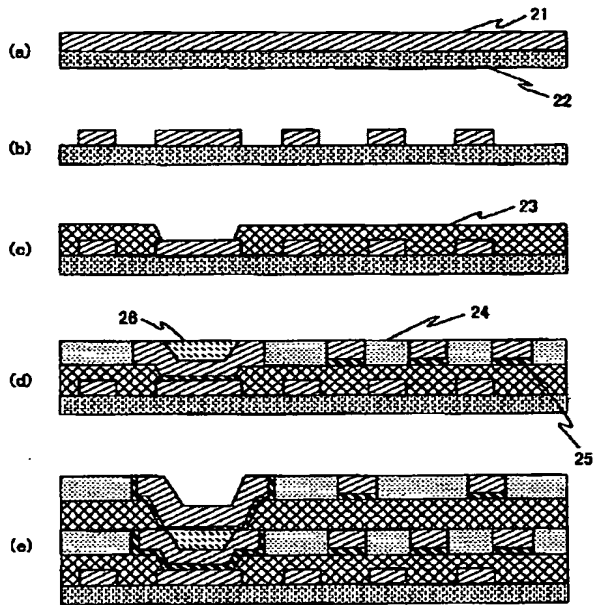


図 4

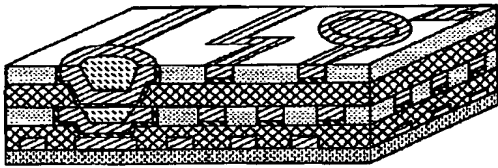
[Drawing 6]

図 6



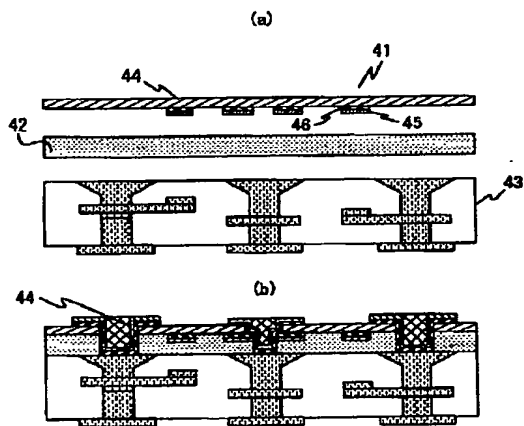
[Drawing 7]

図 7



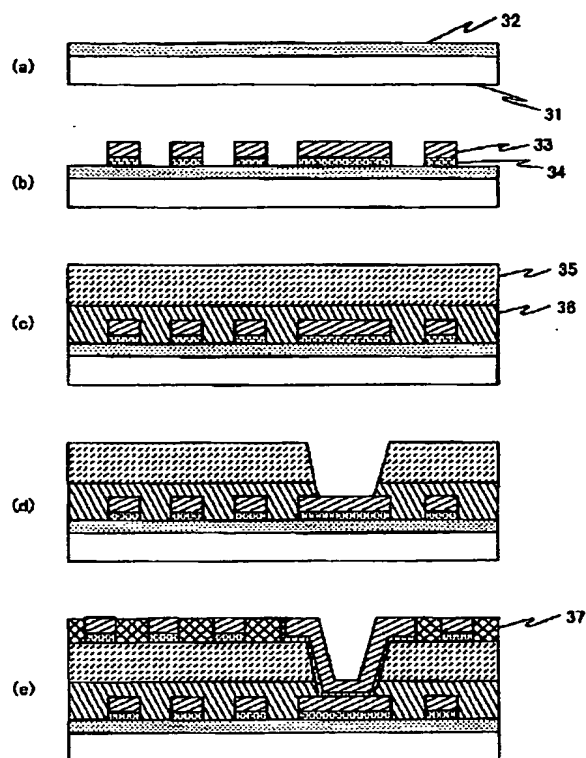
[Drawing 9]

図 9



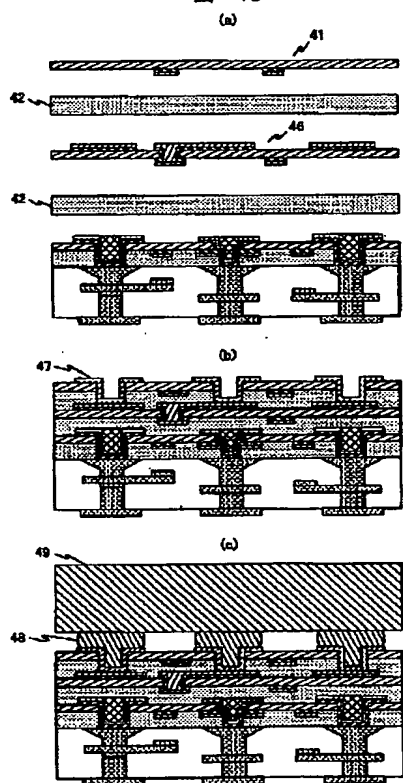
[Drawing 8]

図 8



[Drawing 10]

図 10



[Translation done.]

(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号
特開2000-286559
(P2000-286559A)

(43)公開日 平成12年10月13日(2000.10.13)

(51)Int.Cl. ⁷	識別記号	F I	テマコード(参考)
H 0 5 K 3/46		H 0 5 K 3/46	T 5 E 3 4 3
			B 5 E 3 4 6
3/18		3/18	A
3/38		3/38	A

審査請求 未請求 請求項の数12 O L (全 19 頁)

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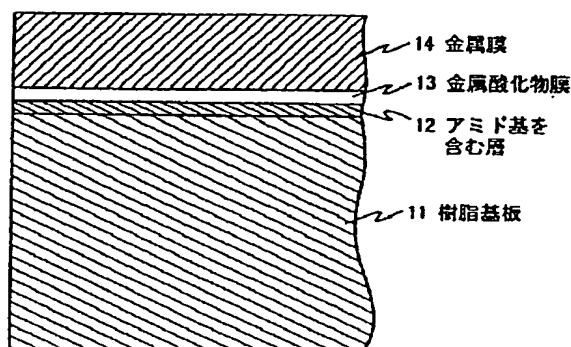
(54)【発明の名称】 配線基板とその製造方法及び半導体装置

(57)【要約】

【課題】本発明の目的は、特に、耐熱性、寸法安定性に優れた絶縁性樹脂基板上に、銅を導体とする配線を密着性の良い無電解めっきによって形成することにより、密着性の高い微細な銅配線を形成する上で極めて有効なフルアディティブ法による配線板製造が可能となり、高密度に実装した配線基板とその製造方法及び用途を提供できる。

【解決手段】本発明は、絶縁樹脂基板として特に耐アルカリ性の高い樹脂を用い、その表面にアミド基を含む層と、銅の還元電位よりも還元電位が卑である金属酸化物層と、銅層とからなる配線基板とその製造方法にある。

図 1



【特許請求の範囲】

【請求項1】絶縁樹脂基板上に該樹脂基板の表面に形成された変質層を介してライン幅が10～40 μm 及び厚さが15～45 μm であるめっき膜からなる配線層が形成され、少なくとも該配線層が形成されている部分の前記基板の中心線平均粗さが1.0 μm 以下であることを特徴とする配線基板。

【請求項2】絶縁樹脂基板上に配線層を有し、該配線層は前記樹脂基板表面に形成されたアミド基を含む変質層及び前記配線層表面に形成された金属酸化物層を含む各層を介して形成されていることを特徴とする配線基板。

【請求項3】絶縁樹脂基板上に配線層を有し、該配線層は前記樹脂基板表面に形成された前記基板表面の中心線平均粗さが0.1～1.0 μm である変質層及び前記配線層表面に形成された金属酸化物層を含む各層を介して形成されていることを特徴とする配線基板。

【請求項4】請求項1～3のいずれかにおいて、前記配線層は前記金属酸化物層表面に触媒層、無電解金属めっき膜及び電気めっき膜が順次積層されて形成されていることを特徴とする配線基板。

【請求項5】請求項2において、前記金属酸化物層は銅の還元電位よりも卑である金属の酸化物からなることを特徴とする配線基板。

【請求項6】請求項4において、絶縁樹脂基板がポリイミド樹脂を含む絶縁樹脂基板であり、前記銅の還元電位よりも還元電位が卑である金属がニッケル、錳、コバルトのうち少なくとも一つを含む金属であることを特徴とする配線基板。

【請求項7】請求項1～6のいずれかにおいて、前記絶縁樹脂基板と配線層とが交互に積層され、前記樹脂基板表面に半導体素子接続用ボンディングパッドを有することを特徴とする配線基板。

【請求項8】セラミックス配線基板上に請求項1～6のいずれかに記載の配線基板が積層され、前記絶縁樹脂基板表面に半導体素子接続用ボンディングパッドが形成されていることを特徴とする配線基板。

【請求項9】請求項7又は8に記載のボンディングパッドに半田によって半導体素子が接続されていることを特徴とする半導体装置。

【請求項10】絶縁樹脂基板上に銅を導体とする配線を設けてなる配線基板の製造方法において、ヒドラジンヒドラートとエチレンジアミンを7対3の割合で混合した液温30℃の混合液に対する溶解速度が1 μm /分以下である樹脂からなる前記絶縁樹脂基板表面にプラズマ処理を施す工程と、前記樹脂基板のプラズマ処理した面に、銅の還元電位よりも還元電位が卑である金属の金属層を無電解めっきにより設ける工程と、前記樹脂基板と接する該金属層との界面に該金属の酸化物層を形成する酸化工程と、前記金属層上に銅層を無電解めっきにより形成する工程を含むことを特徴とする配線基板の製造方

法。

【請求項11】請求項10において、前記プラズマ処理を施す工程、前記樹脂基板のプラズマ処理した面に金属層を設ける工程の間に、該樹脂基板のプラズマ処理を施した面にめっき触媒を付与する工程及びめっきレジストを形成する工程を含むことを特徴とする配線基板の製造方法。

【請求項12】樹脂基板上に銅を導体とする配線が設けられている配線基板の製造方法において、ヒドラジンヒドラートとエチレンジアミンを7対3の割合で混合した液温30℃の混合液に対する溶解速度が1 μm /分以下である樹脂からなる樹脂基板表面を、アルカリ金属水酸化物を含む水溶液で親水化処理を施してアミド基を含む層を形成し、次に、前記アミド基を含む層上に銅の還元電位よりも還元電位が卑である金属膜を形成した後、前記金属膜と前記アミド基を含む層との接触界面の前記金属膜表面に金属酸化膜を形成させる酸化処理を行い、次いで前記金属膜の上に無電解銅めっきを行って銅を形成させることを特徴とする配線基板の製造方法。

20 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、新規な配線基板とその製造方法並びにそれを用いた半導体装置に関する。

【0002】

【従来の技術】近年、LSI技術の高速化、高密度化に伴い、電子回路配線の細線化、多層化、電気特性の更なる向上が要求され、この要求に対して平坦性、耐熱性、寸法安定性や誘電特性に優れた有機絶縁材料を基板に用いた多層配線基板を製造することが検討されている。

30 【0003】有機絶縁樹脂基板上に銅からなる配線を形成する場合、一番問題になるものは、銅配線と樹脂基板との密着性である。従来は、樹脂基板表面をソフトエッチング、あるいは、あらかじめ基板の樹脂の中にゴム成分を入れてそれを溶剤で溶かすなどの方法により樹脂基板表面を粗面化することで、投錨効果あるいは機械的なからみ合い効果により、樹脂基板表面に析出させた金属膜との密着性を向上させるというのが常套手段であった。詳細については、K.L. Mittal 編集 Polymer Surface Modification: Relevance to Adhesion (VSP 出版、1996年)にまとめられている。しかし、この方法では、十分な密着力を得るためには数十ミクロン程度の凹凸が必要であり、数十ミクロン以下のライン幅を持つ微細配線を作ることが困難であった。そこで、配線/スペース幅よりも十分小さい凹凸を表面につくだけで高い密着性をもたらし、かつ、高温下でもその密着性が劣化しない密着促進処理の開発が望まれていた。

40 【0004】有機絶縁樹脂基板上に銅配線を形成する方法として、サブトラクト法とアディティブ法とが知られている。サブトラクト法とは、まず基板全面に銅をメタライズしてから、配線として不必要な部分の銅をエッチ

ングで除去し配線回路を作製する方法である。全面に銅をメタライズする方法としては、CVDやスパッタ法が一般的に用いられている。また、薄付け無電解銅めっきにより基板全面に銅を薄く付け、その後電気銅めっきにより銅を厚付けする方法も提案されており、例えば、特開平4-187778号公報には、ポリイミド樹脂の全面に銅を無電解めっきで $0.3\mu\text{m}$ ほど付け、その後電気銅めっきで $35\mu\text{m}$ ほど厚付けする方法が開示されている。サブトラクト法では、樹脂基板上の $10\mu\text{m}$ 以上の厚みを持つ銅板をエッチングせねばならず、銅配線ラインの側面部もエッチングされることが避けられず、配線ラインの基板に近い側がやせた形状をとることになるため、細いライン・スペースパターンをつくるのが難しく、凡そ $40\mu\text{m}$ 程度のライン・スペースパターンをつくるのが限界であった。

【0005】一方、アディティブ法は、基板上にレジストで回路パターンをつくり、それに沿って導体金属を析出させる方法である。この方法では、銅配線ラインのアスペクト比はほぼレジストの解像度と同等になるため、微細配線の製造に適している。このアディティブ法には、セミアディティブ方式とフルアディティブ方式がある。

【0006】セミアディティブ方式は、基板表面一面にうすく金属を析出させた後めっきレジストを作成し、その後導体金属、多くの場合は銅を電気めっきあるいは無電解めっきで厚付けし、レジストを剥離後下地金属薄膜をエッチアウトすることで配線をつくる方法である。一般的には、銅をエッチアウトした銅張り積層板に銅を無電解めっきでごく薄く付け、レジスト形成後電気銅めっきあるいは無電解銅めっきで厚付けし、レジスト剥離後銅薄膜をエッチアウトする方法が用いられている。しかし、銅をエッチアウトした銅張り積層板のように表面が数十ミクロンの凹凸を持つような基板に対してはこの方法が適用されるが、もっと平滑な基板には、良好な密着性が得られないため、適用できない。より高い密着性を得る目的で、銅以外の金属をまず、基板につけ、そのあと銅を厚付けする方法も提案されている。例えば、特開平10-65061号公報には、絶縁性フィルムに、下地金属層を蒸着法あるいはスパッタリングの乾式めっき法で形成し、その上に無電解銅めっき、つづいて電気銅めっきを行う方法が開示されており、この方法を用いるとセミアディティブ方式で配線基板が製造できる旨記載されている。絶縁性基板上に、下地金属層を設け、その上にレジストを形成した後銅を電気めっきで厚付けし、レジスト剥離後下地金属層をエッチアウトすることでレジスト寸法に近い微細配線が形成される。しかしながら、下地金属と銅が混在している場合、下地金属だけをエッチングすることは一般的に非常に困難である。さらに、下地金属がエッチアウトされると銅配線部とその下の下地金属部では幅が異なることになり絶縁性基板と下地金属層

との間にわずかに隙間が生ずることにある。そうすると、配線基板を絶縁性接着樹脂で積層させる際に、この隙間に接着樹脂が十分に充填されずにボイドとして残るといった問題を生じることとなる。

【0007】一方、フルアディティブ方式は、まず基板にめっき触媒を付与した後めっきレジストを設け、導体金属、たとえば銅を無電解めっきし、必要に応じレジストを剥離するかあるいは永久レジストとして残して配線基板を製造する方法である。下地金属薄膜のエッチアウト工程がないために工程数が少なく、また配線の形状はレジストの形状で決まるため微細配線形成に有利であることからフルアディティブ方式の方が好ましい。さらに、銅以外の下地金属を用いた場合でも、エッチング工程が無く導体部の形状はレジスト形状で決まるためセミアディティブ方式で見られた絶縁性基板と下地金属層との間に隙間が生ずるという問題も発生しない。しかし、樹脂基板に密着性良く無電解銅めっきすることが難しいという問題がフルアディティブ方式の大きな隘路となっていた。強固な密着性を実現するために、樹脂基板を粗面化する方法も提案されているが、 $40\mu\text{m}$ 以下の細いライン・スペースパターンをつくる上で、数十 μm 以上の凹凸を持つ基板を使うことは困難であった。したがって、ライン・スペースパターンの幅に比べ十分小さな凹凸を持つ樹脂基板表面上に、無電解めっき中でも剥離しない強固な密着力を実現する無電解銅めっき方法の開発が求められていた。特開平4-72070号公報には、ポリイミド樹脂基板表面をエッチング処理して触媒付与後無電解銅めっきをし、次いで 120°C 以上の温度で熱処理することで高い密着力が得られることが開示されている。しかし、この公報で開示されている方法では、無電解銅めっきで銅を $1\mu\text{m}$ 以上に厚付けすることはできなかった。

【0008】

【発明が解決しようとする課題】本発明の目的は、密着性の高い微細配線層を有する配線基板とその製造方法及び半導体装置を提供するにある。

【0009】

【課題を解決するための手段】本発明は、絶縁樹脂基板上に該樹脂基板の表面に形成された変質層を介して、ライン幅が $10\sim 40\mu\text{m}$ 、好ましくは $15\sim 35\mu\text{m}$ 及び厚さが $15\sim 45\mu\text{m}$ 、好ましくは $15\sim 35\mu\text{m}$ であるめっき膜からなる配線層が形成され、少なくとも該配線層が形成されている部分の前記基板の中心線平均粗さが $1.0\mu\text{m}$ 以下、好ましくは $0.05\sim 0.3\mu\text{m}$ であることを特徴とする配線基板にある。本発明は、絶縁樹脂基板上に配線層を有し、該配線層は前記樹脂基板表面に形成されたアミド基を含む変質層及び前記配線表面に形成された金属酸化物層を含む各層を介して形成されていることを特徴とする配線基板にある。

【0010】本発明は、絶縁樹脂基板上に配線を有し、

該配線層は前記樹脂基板表面に形成された前記基板表面の中心線平均粗さが $0.1 \sim 1.0 \mu\text{m}$ 、好ましくは $0.3 \sim 0.7 \mu\text{m}$ である変質層及び前記配線表面に形成された金属酸化物層を含む各層を介して形成されていることを特徴とする配線基板にある。

【0011】前記配線層は前記金属酸化物層表面に触媒層、無電解金属めっき膜及び電気めっき膜が順次積層されて形成されていることが好ましい。

【0012】本発明はライン幅を $40 \mu\text{m}$ 以下とする微細配線を密着性を良く形成させるものであり、そのためには絶縁樹脂基板表面の中心線平均粗さを $1.0 \mu\text{m}$ 以下とするものである。このような表面粗さでは従来では高い密着性が得られなかったが、本発明の如く処理を行うことによってこのような微細配線が構成できるものである。更に、ラインスペースパターンにおいても $40 \mu\text{m}$ 以下にでき、好ましくは $10 \mu\text{m}$ 以上であり、より好ましくは $20 \sim 35 \mu\text{m}$ とすることである。このような微細配線はピール強度として 300N/m 以上とすることにより得られ、特にピール強度 (N/m) とライン幅 (μm) とを乗算した値を $10,000$ 以上、好ましくは $15,000$ 以上、より好ましくは $20,000$ 以上であり、ライン幅を小さくするに従ってよりピール強度の高いものとするのが好ましい。また、配線層はライン幅とその厚さとを乗算した値として $400 \sim 1200 \mu\text{m}^2$ とすることが好ましく、より $500 \sim 800 \mu\text{m}^2$ が好ましい。

【0013】本発明は、耐熱性、寸法安定性に優れた樹脂基板表面を改質処理することでアミド基を生成させ、その上に銅の還元電位よりも還元電位が卑である金属を析出させ、両者の界面に該金属の酸化物層を形成した後該金属層上に銅を析出させることで、樹脂基板と銅との密着力を高め、かつその密着性の高温時の劣化を極力抑えた極めて高い信頼を持つ配線基板が得られるものであって、特に樹脂基板上に数十ミクロン以下のライン幅を持つ微細銅配線を形成するうえで極めて有効なフルアディティブ方式により樹脂基板上に銅配線を形成するものである。

【0014】発明者らは、どのような化学的な相互作用が樹脂基板と析出させる金属との密着力を高めるかについて鋭意検討した結果、アミド基と金属酸化物膜との間に非常に強く相互作用が働くことを見いだした。

【0015】本発明は、絶縁樹脂基板と、該樹脂基板上に析出された金属膜と、該金属膜と前記樹脂基板との接触界面の前記樹脂基板側表面に形成されたアミド基を含む層と、前記接触界面の前記金属膜側表面に形成された金属酸化物膜とで構成され、前記金属膜を導電体とする配線が前記樹脂基板上に設けられていることが好ましい。

【0016】また、本発明は、絶縁樹脂基板上に銅を導体とする配線を設けてなる配線基板において、前記絶縁

樹脂基板上に、該絶縁樹脂基板表面をプラズマ処理を施すことによって形成される変質層と、銅の還元電位よりも還元電位が卑である金属の金属酸化物層と、該金属の金属層と、銅層を順次積層した構造をとることが好ましい。

【0017】また、本発明は、銅の還元電位よりも還元電位が卑である金属がニッケル、錫、コバルトのうち少なくとも一つを含む金属であることが好ましい。

【0018】本発明は、絶縁樹脂基板上に銅を導体とする配線を設けてなる配線基板の製造方法において、ヒドラジンヒドラートとエチレンジアミンを7対3の割合で混合した混合液に対する溶解速度が、液温 30°C のもとで、 $1 \mu\text{m}/\text{分}$ 以下である樹脂からなる樹脂基板表面にプラズマ処理を施す工程と、前記樹脂基板のプラズマ処理した面に、銅の還元電位よりも還元電位が卑である金属の金属層を無電解めっきにより設ける工程と、前記樹脂基板と接する該金属層との界面に該金属の酸化物層を形成する工程と、前記金属層上に銅層を無電解めっきにより形成する工程を含むことを特徴とする。

【0019】また、本発明は、絶縁樹脂基板にプラズマ処理を行う際に、反応ガスとして酸素あるいは窒素を用い、処理表面の中心線平均粗さが $0.1 \mu\text{m}$ 以上かつ $1.0 \mu\text{m}$ 以下となるようにプラズマ処理を行ったことが好ましい。

【0020】また、本発明は、樹脂基板にプラズマ処理を施す工程と、前記樹脂基板のプラズマ処理した面に金属層を設ける工程の間に、該樹脂基板のプラズマ処理を施した面にめっき触媒を付与する工程とめっきレジストを形成する工程を含むことが好ましい。

【0021】また、本発明の配線基板は、絶縁樹脂層上に金属導体からなる配線を設けた配線樹脂層を複数層積層してなり、表面に開口部を有し、該開口部内でICと電氣的に接続するためのボンディングパッドを有する配線基板において、ヒドラジンヒドラートとエチレンジアミンを7対3の割合で混合した混合液に対する溶解速度が、液温 30°C のもとで、 $1 \mu\text{m}/\text{分}$ 以下である樹脂からなる樹脂層と、ニッケル、錫、コバルトのうち少なくとも一つを含む第一金属層と、該第一金属層に含まれる金属とは異なる第二金属層を順次積層した構成からなる導体を有することを特徴とする。

【0022】また、本発明は、セラミックを絶縁層の成分とするセラミック配線基板と、樹脂を絶縁層の成分とする樹脂配線基板を積層し、両者を電氣的に接続した構成をもつ配線基板において、前記樹脂配線基板が、ヒドラジンヒドラートとエチレンジアミンを7対3の割合で混合した混合液に対する溶解速度が、液温 30°C のもとで、 $1 \mu\text{m}/\text{分}$ 以下である樹脂からなる絶縁層と、ニッケル、錫、コバルトのうち少なくとも一つを含む第一金属層と、該第一金属層に含まれる金属とは異なる第二金属層を順次積層した構成からなる導体を有することを特

徴とする。

【0023】また、本発明は、樹脂基板上に銅を導電体とする配線が設けられている配線基板の製造方法において、ヒドラジンヒドレートとエチレンジアミンを7対3の割合で混合した混合液に対する溶解速度が、液温30℃のもとで、1μm/分以下である樹脂からなる樹脂基板表面を、アルカリ金属水酸化物を含む水溶液で親水化処理を施してアミド基を含む層を形成し、次に、前記アミド基を含む層上に、銅の還元電位よりも還元電位が卑である金属膜を析出させ、次に、前記金属膜と前記アミド基を含む層との接触界面の前記金属膜表面に金属酸化膜を形成させ、その後、前記金属膜の上に無電解銅めっきを行って銅を析出させることを特徴とする。

【0024】図1は、本発明の配線基板の断面構成図である。樹脂基板上の金属を1種類とする場合には、樹脂基板と金属層との界面の、樹脂基板側にはアミド基を含む層あるいはプラズマ処理を施すことによって形成される変質層があり、金属層側には、金属の酸化物層がある。また、樹脂基板上の金属を1種類以上とする場合には、該金属層上に第二の金属層が形成されている。特に、第二の金属が銅であり、銅を無電解めっきにより形成する場合には、第一の金属は、銅の還元電位よりも還元電位が卑である金属である。

【0025】本発明に係る耐熱性の高い絶縁樹脂基板としては、ポリアミド樹脂、ポリイミド樹脂、ポリベンゾオキサゾール、ポリアミドイミド樹脂、ポリベンズイミダゾール樹脂、アラミド樹脂、エポキシ樹脂などが挙げられる。特に、無電解銅めっきで厚付けを行う場合には、ヒドラジンヒドレートとエチレンジアミンを7対3の割合で混合した混合液に対する溶解速度が、液温30℃のもとで、1μm/分以下であるという条件をみたすものが好ましい。

【0026】骨格中にアミド基を含み耐熱性の高い樹脂としては、ポリアミド樹脂、ポリアミドイミド樹脂などが挙げられる。また、薬品で表面処理することにより表面にアミド基を導入できる耐熱性樹脂としては、酸無水物とアミンを脱水縮合させてつくるポリイミドや、ポリアミドを加熱して脱水させてつくるポリベンゾオキサゾール等を挙げることができる。アミド基になる官能基を持たない樹脂、例えばポリエチレンやエポキシ樹脂などの場合には、まず、強酸処理で表面にカルボキシル基を導入し、それをアミンと反応させることによりアミド基を生成することができる。アミド基を生成する表面改質処理を施した後あるいはプラズマ処理を行った後のその上につける金属との密着力を評価するとポリイミド樹脂が特に高い密着力を示した。このことから、樹脂基板としては特にポリイミド樹脂が好ましい。

【0027】一般に、プラズマ処理の場合、表面形状は、使用される反応ガスの種類に依存する。しかし、密着性は、使用する反応ガスが酸素の場合でも窒素の場合

でも、変質層表面の中心線平均粗さが、0.1μm以上であった場合に高く、90度の引き上げピール試験におけるピール強度として、25℃のもと500N/m以上の実用プロセスに耐えうる密着強度が得られた。このことから、反応ガスとしては、酸素及び窒素が好ましく、形成されるアミド基を含む変質層表面の中心線平均粗さが0.1μm以上になるようにプラズマ処理されることが密着性の点から好ましい。一方、中心線平均粗さが、1.0μm以上になるほど樹脂基板表面が粗面化されると、ライン/スペースとして10~40μm、好ましくは15~30μm、特に20μm程度の微細配線をつくるときに配線の凹凸が無視できなくなり、また変質層自身が脆くなるという問題を生じる。したがって、中心線平均粗さは、0.1μm以上かつ1.0μm以下より0.15~0.35μmが望ましい。

【0028】銅の還元電位よりも還元電位が卑である金属としてはニッケル、コバルト、チタン、クロムを挙げることができる。金属層及び銅の析出方法としては、スパッタ法を用いることもできるが、微細配線形成に適しているフルアディティブ法を用いて配線パターンを作製するためには無電解めっきを用いることが好ましい。前記金属の酸化物層は、あらかじめ前記金属を樹脂基板上に薄く析出させた後酸化処理を施すことで形成する。あるいは、樹脂基板の一方の面にのみ前記金属を析出させた後、酸素雰囲気におくことで樹脂基板を通して界面に酸素を供給することで金属酸化物層を形成することができる。アミド基生成処理した樹脂基板表面と金属酸化物層との相互作用を引き起こすためには両者が接していればよく、両者の厚みには特に関係しない。

【0029】最上層の銅は、スパッタ法で形成することや電気めっきで形成することもできるが、フルアディティブ法で配線基板をつくる上では、無電解めっきで形成することが好ましい。

【0030】配線パターンの作製には、樹脂基板全面に金属を析出させた後適当なレジストを用いてエッチングによって配線パターンをつくるいわゆるサブトラクト法や、樹脂基板全面に金属膜を薄くつけてからレジストをはり電気めっきあるいは無電解めっきにより金属を厚付けした後不要な部分の薄付け金属膜をエッチアウトするいわゆるセミアディティブ法や、樹脂基板にレジストをはってから無電解めっきにより金属を厚付けして導体配線をつくるいわゆるフルアディティブ法などを用いることができる。

【0031】フルアディティブ法で配線基板をつくるプロセスとしては、次のようなプロセスも考えられる。プラズマ処理を施した樹脂基板全面に、めっき用触媒を付与した後に、樹脂基板表面に感光性ドライフィルムをラミネートしあるいは感光性絶縁樹脂塗液を塗工乾燥し、露光、現像することでめっきレジストを形成する。必要に応じて、後露光、後加熱を行う。その後、無電解めっき

でまず銅の還元電位よりも還元電位が卑である金属の金属層を形成する。この金属層形成後加熱処理を行うことで樹脂基板/該金属層界面に該金属の酸化物層を形成する。その後、該金属層表面の酸化物層を希塩酸等で除去した後、無電解銅めっき浴に入れ銅を所望の厚さだけめっきし銅配線基板を完成させる。

【0032】配線層を積層する方法としては、絶縁樹脂の塗液を導体配線の上に塗工、乾燥する工程と導体配線を形成する工程を順次繰り返す方法が上げられる。必要に応じ、絶縁層を研磨し平坦化する。また、絶縁層として絶縁樹脂のフィルムを用いる場合には、樹脂フィルム上に導体配線を形成し、導体配線シートを作り、適切な接着材シートを挟んで別の導体配線シートを重ね、加熱、加圧することで積層することができる。各層間の電気的な接続は、レーザ光を用いたビアホール形成と、ビアホール内のめっきあるいは導電ペーストの充填等により容易に実現できる。

【0033】本発明の配線基板は、用いる目的によって、それ自身単独でフレキシブル配線基板として用いることもできるし、セラミック板、ガラス板、シリコンウエハなどの上に設けることによって剛性のある配線基板として用いることもできる。また、セラミック配線基板上に本発明の配線基板を設け、両者の電気的な接続をとることで一体の配線基板として用いることもできる。さらに、本発明の配線基板は、表面に複数のICを搭載することが容易にできることから、マルチチップモジュール基板として用いることができる。特に、フルアディティブ方式で微細銅配線を形成できることから、複数のICを実装するマルチチップモジュール基板として適している。

【0034】本発明者らは、特定の官能基と金属の酸化物とが密着性を高めることを見いだした。

【0035】ポリイミドをアルカリ水溶液で処理すると表面近傍のイミド環が開環し、アミド基ができることを全反射赤外吸収スペクトル測定から確かめた。ポリイミドとしてデュボン社製カプトン200Hを使った場合の処理前後の全反射赤外吸収スペクトルを図2に示し、また、その差スペクトルを図3に示す。表面処理により1650、1550 cm^{-1} 付近に新たな吸収帯が現れているが、それぞれアミドI及びアミドII吸収帯に帰属される。このスペクトル変化から、イミド環が開環しアミド基ができていることが分かる。この表面に、めっき用触媒(日立化成社製HS-101B)を付与し、無電解銅めっき液(日立化成社製CUST-2000)を用いて銅めっきを行った。めっき液の温度は40度、めっき時間は3秒であり、めっき後真空乾燥により十分乾燥した後一日空气中に放置した。めっき前後の前記差スペクトルの変化を図4に示す。アミドI及びアミドII吸収帯にめっき前後で明瞭な変化が見られた。この変化は、明らかに、アミド基とめっき銅めっき膜との相互作用の存在を

示している。

【0036】そこで、表面処理したポリイミドに上記無電解銅めっきで銅膜を約30nmほど付け、それを電気銅めっきで銅を約20 μm ほど厚付けし、ピールテストで密着性を評価した。電気銅めっき直後はピール強度がほとんどないが、それを空气中に放置しておいたところ、時間とともに密着性が著しく向上した。特に、電気銅めっき後真空乾燥した後酸素雰囲気下に放置した場合にピール強度の増加が著しかった。ピール強度の経時変化を図5に示す。この結果は、明らかに、ポリイミドとめっき銅膜との界面に銅の酸化物膜ができると両者の密着性が著しく向上することを示している。したがって、アミド基と銅の酸化物との間には非常に強い相互作用が働き、密着力が発現することが分かる。このような結果は、他の種類のポリイミドや銅以外の金属、たとえばニッケル、コバルト、チタンなどの組み合わせの場合についても同様であった。また、この結果は、単にポリイミド樹脂だけに限られたものではなく、他の樹脂、例えば、ポリベンゾオキサゾール樹脂、ポリベンズイミダゾール樹脂等でも観測された。つまり、加水分解により樹脂表面にアミド基を導入すれば同じ結果が得られることが分かった。

【0037】また、本発明者らは、プラズマ処理によって形成される変質層も、上記アミド基を含む層と同様に金属酸化物との間に非常に強い相互作用が働いていること、そのため非常に高い密着力が得られることをピールテストより明らかにした。

【0038】さらに、本発明者らは、樹脂材料表面にアミド基を導入する処理あるいはプラズマ処理を施し、銅の還元電位よりも還元電位が卑である金属の金属層を形成した後界面に該金属の酸化物層を形成することで飛躍的に樹脂材料と該金属層との密着性が向上すること、また、このように密着性が高い界面をつくった後、この金属層の上に銅を無電解めっきで厚付けすることができることを見いだした。

【0039】ポリイミド樹脂を配線基板に用いる基板材料としては、耐熱性、寸法安定性、誘電特性等に優れた樹脂材料が適しているが、特に大切な点は、耐アルカリ性が高いことである。無電解銅めっき浴では、ホルムアルデヒドなどの還元剤が金属銅表面で酸化する反応が起きる必要があるが、その反応がおきるためにはアルカリ性でなければならず、したがって、配線基板材料はアルカリ性の液に長時間曝されることになる。耐アルカリ性が低いと、無電解銅めっき中に土台となる基材が溶け、銅めっき膜が剥離することが観測された。そこで、耐アルカリ性と耐無電解銅めっき浴性との関係を検討した。耐アルカリ性の指標として、液温30℃のヒドラジンヒドラート/エチレンジアミン(70/30、重量比)混合液中におけるエッチング速度を用いた。樹脂としては、ジアミンと酸無水物との組み合わせで種々の構造を

持つ高分子が得られるポリイミドを選んだ。その結果、エッチング速度が $1\mu\text{m}/\text{分}$ 以下であれば、液温 70°C 、 $\text{pH}12$ 程度の無電解銅めっき浴中で 15 時間以上めっきをしても基板上に析出させためっき膜が剥離しないことが確かめられた。この条件は、単にポリイミド樹脂だけに限定されるものではなく、他の樹脂、例えば、ポリベンゾオキサゾール、ポリアミド樹脂、ポリアミドイミド樹脂、ポリベンズイミダゾール樹脂、アラミド樹脂、エポキシ樹脂等でも適用できることが分かった。

【0040】次に、上記樹脂基板表面を無電解銅めっきでめっきする際、銅と樹脂基板との間に十分な密着力を得る方法について鋭意検討した。種々の条件で基板表面を改質し、その後銅をスパッタリングで約 $1\mu\text{m}$ 蒸着し、その後電気銅めっきで膜厚を $20\mu\text{m}$ になるまで厚付けしてピール強度を評価した。その結果、樹脂基板表面をアルカリ溶液で処理する方法、また酸素あるいは窒素を反応ガスとするプラズマ処理を行う表面処理方法が有効であることが判明した。特に、プラズマ処理の場合には、樹脂基板表面に中心線平均粗さ(R_a)で $0.1\mu\text{m}$ 以上の凹凸を形成する処理条件が特に高い密着性をもたらす、例えば、 25°C のもと、 90 度の引き上げピール試験におけるピール強度として $500\text{N}/\text{m}$ 以上の、実際の配線基板製造プロセスに耐えうる密着力が得られるようになった。

【0041】上記表面改質処理を施した樹脂基板に、めっき用触媒を付与し無電解銅めっき浴に入れめっきを行ったところ、 pH の値($10-13$)、めっき浴の温度($20-80^\circ\text{C}$)に関わらず、銅の膜厚約 30nm 以下の段階でめっき膜が剥離してしまった。薄付け用のフラッシュ無電解銅めっきを行った後厚付け用の無電解銅めっきを行った場合にも厚付け用無電解銅めっき開始直後めっき膜が剥離してしまい厚付けができなかった。したがって、改質処理を行った樹脂基板表面と銅との密着力は、無電解銅めっき浴中で著しく低下することが分かった。そこで、銅以外の金属膜を樹脂基板表面につけてから無電解銅めっきを行うことを種々検討した。その結果、ニッケル、錫、コバルト等の金属膜をつけてから無電解銅めっきを行うとめっき中でのめっき膜の剥離が起これなくなることを見いだした。金属の種類を種々検討した結果、銅の還元電位よりも還元電位が卑である金属をあらかじめつけておくことが有効であることを見いだした。同時に、樹脂基板に金属膜をつけた後、それを酸化雰囲気におくことで樹脂基板と金属膜との間で金属の*

〔表面改質処理水溶液組成〕

- ・水酸化ナトリウム
- ・エチレンジアミン
- ・エタノール

処理した試料片をガラスクロス入りエポキシ樹脂基板に貼り付け、 25°C のもと 3 時間真空乾燥を行った。その後、試料片の表面をゲルマニウムブリズムに押しあて全

* 酸化膜を形成させることで樹脂基板と金属膜との密着強度が著しく向上することを見いだした。例えば、ポリイミド樹脂基板表面をアルカリ溶液で処理し、その上にニッケルを無電解めっきで膜厚 $1\mu\text{m}$ ほどつけ、電気銅めっきでニッケルの上に銅を膜厚 $20\mu\text{m}$ ほど厚付けしてポリイミド/ニッケル間の密着性を評価したところ、ニッケルめっき後に大気中 180°C で 2 時間アニール処理した試料と処理していない試料のピール強度を比較すると、各々 $900\text{N}/\text{m}$ 、 $300\text{N}/\text{m}$ という値が得られた。このようなめっき後のアニールによる密着性の向上は、樹脂の表面処理としてプラズマ処理を行った場合にも観測された。このことは、接着界面における酸化物がアミド基を有する樹脂表面やプラズマ処理された樹脂表面と化学的な相互作用を持つためと思われる。

【0042】以上のことから、樹脂基板として、ヒドラジンヒドラートとエチレンジアミンを 7 対 3 の割合で混合した混合液に対する溶解速度が、液温 30°C のもと、 $1\mu\text{m}/\text{分}$ 以下である樹脂基板を用い、樹脂基板表面にアミド基を導入する処理を行うかあるいはプラズマ処理を施し、処理面に銅の還元電位よりも還元電位が卑である金属の金属層を設け、前記樹脂基板と接する該金属層との界面に該金属の酸化物層を形成することで、前記金属層上に銅膜を無電解銅めっきで厚付けできることを見いだし、本発明を完成するに至った。

【0043】さらに、アミド基導入処理あるいはプラズマ処理を施した樹脂基板上に、触媒を付与した後ドライフィルムをラミネートした後露光、現像によりめっきレジストを形成し、例えばニッケルを無電解めっきで付けた後、大気中ベーク処理を行って樹脂基板/ニッケル界面にニッケル酸化膜を形成し、表面のニッケル酸化膜を除去した後無電解銅めっき浴に入れて銅を厚付けすることで、樹脂基板上に $20\mu\text{m}$ 程度のなライン・スペースパターンを持ち、膜厚が $20\mu\text{m}$ 程度の微細かつ高アスペクト比の銅配線をつくることを見いだすに至った。

【0044】

〔発明の実施の形態〕(実施例1) 表面粗さが $0.1\mu\text{m}$ 以下であるデュボン社製カプトン 200H のポリイミドフィルムの樹脂基板に用いた。 $10\text{cm}\times 10\text{cm}$ の試料片を作り、液温 25°C の表面改質処理水溶液で 2 分間処理した。

【0045】

$100\text{g}/\text{l}$

$70\text{g}/\text{l}$

$100\text{g}/\text{l}$

反射赤外吸収測定したところ、イミド環のカルボニル基に帰属される 1780cm^{-1} と 1720cm^{-1} 付近の吸収ピークに加えて 1650cm^{-1} と 1550cm^{-1} 付近にアミド

基特有の吸収ピークが観測された。このことから、この表面処理によりアミド基が表面に導入されたことが確認された。この試料片に、日本鉱業社製サーキットブレッダー3040、3340及び4041を用いて所定の方法でめっき用触媒処理を行った。次に、日立化成社製CUST-2000薄付け用無電解銅めっき液を用いてめっきを行った。膜厚は約30nmであった。流水で水洗後、25℃のもと3時間真空乾燥を行った。次に、試料*

[電気銅めっき液組成]

- ・ 硫酸銅5水和物
- ・ 硫酸
- ・ 塩化ナトリウム

電気銅めっき後、流水で十分洗浄した後25℃のもと3時間真空乾燥を行った。試料をガラスクロス入りエポキシ樹脂基板からはがし、銅膜側を両面テープにてシリコンウエハに固定してポリイミドフィルム側を引き剥がすピールテストを行った。ピールテスト時の剥離界面は、ポリイミドと銅膜の界面で剥離していた。ピール強度は、1.2kN/mと非常に高い密着力が得られた。また、この基板試料を窒素雰囲気中300℃で1時間放置した後のピール強度は約1.1kN/mとほとんど変化していなかった。さらに、この基板試料を150℃の大気中で1000時間保持した後、ピール試験を行ったところピール強度は約0.9kN/mと非常に高い密着強度を保っていた。このことは、この基板を電子部品として使用した場合に熱的安定性において非常に信頼性が高いことを示している。

【0047】(実施例2)ポリイミドフィルムとしてデュボン社製カプトン200Hを用いた。10cm×10cmの試料片を作り、これを実施例1で用いたものと同じ表面改質処理水溶液で液温25℃のもと2分間処理した。処理後、試料片をガラスエポキシ樹脂基板に貼り付け、日本鉱業社製サーキットブレッダー3040、3340及び4041を用いて所定の方法でめっき用触媒処理を行った。次に、無電解ニッケルめっき液(奥野製薬社製B-1)でニッケルを膜厚約0.1μmほどつけた。めっき後、試料をガラスエポキシ樹脂基板からはがし、40℃に加熱しながら3時間真空乾燥した後、酸素気流下に1時間置いた。試料のポリイミドフィルム側から低角でX線を照射して回折スペクトルを測定し、ポリイミドフィルムとニッケル膜との界面を調べ、界面にニッケルの酸化物が存在していることを確かめた。その後、電気銅めっきでニッケル膜の上に銅を膜厚約20μmほど厚つけた。用いた電気銅めっき液及びめっき条件は実施例1と同じである。電気めっき後、試料を40℃に加熱しながら3時間真空乾燥した後、酸素気流下に1時間置いた。その後、実施例1と同様な方法によりピールテストを行った。その結果、ピール強度は約1.6kN/mと非常に高い密着力を示した。また、この基板試料を窒素雰囲気中300℃で1時間放置した後のピール強度は約

*を酸素気流下に1時間置いた。試料の樹脂基板側から低角でX線を照射して回折スペクトルを測定して樹脂基板と銅膜との界面を調べ、界面に銅酸化物が存在していることを確かめた。その後、銅膜上に電気銅めっきを電流密度15mA/cm²として膜厚約20μmほど厚つけた。

【0046】

0.80モル/l

0.54モル/l

0.0014モル/l

1.5kN/mとほとんど変化していなかった。さらに、この基板試料を150℃の大気中で1000時間保持した後、ピール試験を行ったところピール強度は約1.3kN/mと非常に高い密着強度を保っていた。このことは、この基板を電子部品として使用した場合に熱的安定性において非常に信頼性が高いことを示している。

20 【0048】(実施例3)ポリイミドフィルムのデュボン社製カプトン200Hを樹脂基板に用いた。5cm×5cmの試料片を4枚作り、これらを液温25℃の実施例1に記載した表面改質処理水溶液で2分間処理した。

【0049】処理後、試料片をガラスクロス入りエポキシ樹脂基板に貼り付け、25℃のもと3時間真空乾燥を行った。その後、試料片に、各々コバルト、スズ、銅、ニッケルを約1μmほどスパッタした。次に、試料をエポキシ樹脂基板からはがし、酸素気流下に1時間置いた。これらの試料のポリイミドフィルム側から低角でX線を照射して回折スペクトルを測定してポリイミドフィルムと金属膜との界面の状態を調べ、いずれの金属試料の場合にも界面に酸化物が存在していることを確かめた。その後、各スパッタ金属膜上に実施例1と同じ条件で電気銅めっきで銅を膜厚約20μmほど厚つけた。

【0050】電気銅めっき後、25℃のもと3時間真空乾燥を行った。銅膜を両面テープにてシリコンウエハに固定し、ポリイミドフィルム側を引き剥がすピールテストを行った。ピールテスト時の剥離界面は、いずれの試料の場合にも、ポリイミドと各種金属膜の界面で剥離していた。コバルト、スズ、銅、ニッケルの各試料のピール強度は、各々1.5、1.4、1.2、1.6kN/mと非常に高い密着力が得られた。また、これらの基板試料を窒素雰囲気中300℃で1時間放置した後のピール強度は各々1.4、1.4、1.0、1.5kN/mとほとんど変化していなかった。さらに、これらの基板試料を150℃の大気中で1000時間保持した後、ピール試験を行ったところピール強度はいずれの場合にも約0.8kN/m以上と非常に高い密着強度を保っていた。このことは、これらの基板を電子部品として使用した場合に熱的安定性において非常に信頼性が高いことを示してい

る。

【0051】(実施例4) 9.1 重量部の4, 4'-ジヒドロキシ-m-ベンジジンを50重量部のジメチルアセトアミド/ピリジン混合溶媒(重量比1:1)にとかし、10重量部の塩化イソフタロイルを50重量部のシクロヘキサノンに溶かした。後者の溶液を前者の溶液に非常にゆっくりと滴下した。生成した固形分を分離し、これをN-メチルピロリドンに溶解させ、このワニスの粘度を50ボイズ程度に調整し、10 μ mのメンブランフィルタを用いて加圧濾過を行い微小な不溶成分を除去した。このワニスをガラス板にスピンコート法により塗布し、100℃で1時間加熱した後ガラス基板から剥がしてフィルムを得た。フィルムの膜厚は40 μ mであった。次に、このフィルムを鉄棒で固定した後窒素ガス雰囲気下で100℃から400℃まで90分で連続昇温し、脱水縮合反応を行わせてポリベンゾオキサゾールフィルムを得た。このフィルムから10cm \times 10cmの試料片を作り、これを実施例1に記載した表面改質処理水溶液で液温70℃、5分間処理した。処理後、試料片表面に台形型ゲルマニウムプリズムを押しつけ多重反射ATR法により表面の赤外吸収スペクトルをFT-IR測定装置(パーキンエルマー社製システム2000)により測定し、表面にアミド基が生成していることを確かめた。試料片をガラスエポキシ樹脂基板に貼り付け、実施例1に記載したと同様な処理方法でめっき用触媒処理を行った。つぎに、実施例1と同様に日立化成社製無電解銅めっき液CUST-2000で液温40℃のもとで2分間めっきした。めっき膜の厚みは約30nmであった。試料をガラスエポキシ樹脂基板からはがし、40℃に加熱しながら3時間真空乾燥した後、酸素気流下に1時間置いた。試料の樹脂基板側から低角でX線を照射して回折スペクトルを測定して樹脂基板と銅膜との界面の状態を調べ、界面に銅酸化物が存在していることを確かめた。その後、電気銅めっきで銅を膜厚約20 μ mほど厚づけした。用いた電気銅めっき液の組成及びめっき条件は実施例1と同じである。樹脂フィルム側を両面テープにてシリコンウエハに固定し、銅膜を引き剥がすピールテストを行った。その結果、ピール強度は約1.1kN/mと非常に高い密着力が得られた。また、この基板試料を窒素雰囲気中300℃で1時間放置した後のピール強度は約1.0kN/mとほとんど変化していなかった。さらに、この基板試料を150℃の大気中で1000時間保持した後、ピール試験を行ったところピール強度は約0.9kN/mと非常に高い密着強度を保っていた。このことは、この基板を電子部品として使用した場合に熱的安定性において非常に信頼性が高いことを示している。

【0052】(実施例5) ガラスクロス入りエポキシ基板を、ドライエッチング装置(アネルバ社製、DEA-506)を用いて酸素プラズマ処理を行った。処理条件

は、圧力3Pa、流量25SCCMである。プラズマの出力は800Wとし、45分間処理した。その後、液温50℃のクロム酸硫酸混合水溶液(CrO₃ 5部、硫酸100部、水10部)で5分間処理した後水洗し、エチレンジアミンで5分間浸漬処理し、十分水洗した。処理後のエポキシ基板表面を全反射赤外吸収測定したところ、1650cm⁻¹と1550cm⁻¹付近にアミド基に同定される吸収ピークが観測されたことから、これらの処理により表面にアミド基が導入されたことを確認した。この処理基板を3枚用意し、その上に、ライン/スペースが5mm/5mm間隔で形成されているマスクをととして、各々チタン、クロム、タングステン薄膜(膜厚約50nm)をスパッタで成膜した。その後、試料を180℃で2時間加熱処理を行い、エポキシ樹脂基板と各種金属膜との界面に各種金属の酸化膜を形成した。実施例1と同じ条件で電気銅めっきで各種金属膜上に銅を20 μ m付けした。次に、銅膜を引き剥がすピールテストを行った。ピールテスト時の剥離界面は、いずれの試料の場合にも、エポキシ基板と各金属膜の界面で剥離していた。チタン、クロム、タングステンの各試料のピール強度は、各々0.7、0.6、0.6kN/mと、いずれの金属の場合にも高い密着力が得られた。また、これらの基板試料を窒素雰囲気中300℃で1時間放置した後のピール強度はほとんど変化していなかった。さらに、これらの基板試料を150℃の大気中で1000時間保持した後、ピール試験を行ったところピール強度はいずれも0.5kN/m以上と比較的高い密着強度を保っていた。このことは、これらの基板を電子部品として使用した場合に熱的安定性において信頼性が高いことを示している。

【0053】(比較例1) ポリイミドフィルムとして実施例1と同じデュボン社製カプトン200Hを用いて10cm \times 10cmの試料片を作り、ガラスエポキシ樹脂基板に貼り付けた後十分流水で水洗し、めっき触媒付与工程、無電解銅めっき工程までを実施例1と同様に行った。めっき膜の厚みは約30nmであった。めっき後、直ちに試料をガラスエポキシ樹脂基板からはがし、実施例1と同様な条件で銅を電気銅めっきで厚づけした。めっき開始後約10分程度で銅めっき膜の一部が端から剥離しはじめ、約30分ほどでめっき膜全体が剥離してしまった。

【0054】(比較例2) ポリイミドフィルムとして実施例1と同じデュボン社製カプトン200Hを用いて10cm \times 10cmの試料片を作り、ガラスエポキシ樹脂基板に貼り付けた後十分流水で水洗し、表面処理工程、めっき触媒付与工程、無電解銅めっき工程までを実施例1と同様に行った。めっき膜の厚みは約30nmであった。めっき後、直ちに試料をガラスエポキシ樹脂基板からはがし、実施例1と同様な条件で銅を電気銅めっきで膜厚約20 μ mほど厚づけした。銅のめっき膜の一部が、電

気めつき中に端から剥離した。めつき後に、剥離していない部分のピール強度を実施例1と同様に測定したところ、約30N/m程度と非常に弱い密着力しか得られなかった。試料を窒素ガスを充填したグローブボックス中でポリイミドフィルムと銅めつき膜に剥離させ、銅めつき側表面のX線回折を調べたところ、界面に銅酸化物の存在は認められなかった。

【0055】(比較例3) ポリイミドフィルムとして実施例1と同じデュボン社製カプトン200Hを用いて10cm×10cmの試料片を作り、ガラスエポキシ樹脂基板に貼り付けた後十分に流水で洗浄し、表面処理は行わずに、実施例1に記載したと同様な処理方法でめつき用触媒処理を行った。次に、実施例1に記載したと同様な方法で無電解銅めつきを行い、銅を膜厚約30nmほどつけた。流水で水洗後、25℃のもと3時間真空乾燥を行った。次に、試料を酸素気流下に1時間置いた。試料のポリイミド側から低角でX線を照射して回折スペクトルを測定し、樹脂基板と銅膜との界面の状態を調べたところ、界面に銅酸化物が存在していることが分かった。その後、実施例1と同様に銅薄膜上に電気銅めつきで銅を膜厚約20μmほど厚づけた。電気銅めつき後、流水で十分洗浄した後25℃のもと3時間真空乾燥を行った。試料をガラスクロス入りエポキシ樹脂基板からはがし、銅膜側を両面テープにてシリコンウエハに固定してポリイミドフィルム側を引き剥がすピールテストを行った。ピールテスト時の剥離界面は、ポリイミドと銅膜の界面で剥離していた。ピール強度は、0.1kN/mと非常に低い密着力しか得られなかった。

【0056】以上のことから、樹脂と金属との界面で高い密着力を得るには、樹脂表面にアミド基が存在すると金属側では界面部分に酸化膜が存在することが必要であるといえる。

【0057】(実施例6) ポリイミドフィルムからなる樹脂基板として宇部興産社製ユービレックス25Sを用いた。10cm×10cmの試料片を2枚作り、これらをドライエッチング装置(アネルバ社製、DEA-506)を用いて酸素プラズマ処理を行った。処理条件は、出力800W、処理時間25分、圧力3Pa、流量25SCCMである。処理した試料片をガラスエポキシ樹脂基板に貼り付け、実施例1に記載したと同様な処理方法でめつき用触媒処理を行い、つぎに、無電解ニッケルめつき液(奥野製薬社製B-1)でニッケルを膜厚約1μmほどつけた。その後直ちに、実施例1と同様なめつき条件で電気銅めつきを行い銅をニッケル膜の上に膜厚約20μmほど厚づけた。その後、一つの試料を真空乾燥機に入れ、真空中、180℃で2時間ベークした。もうひとつの試料は、大気中で同じ180℃で2時間ベークした。ベーク後、2つの試料の銅膜がついている側を両面テープにてシリコンウエハに固定し、25℃のもと、ポリイミドフィルムを90度上方に引き上げて引き剥がす

ピールテストを行った。その結果、真空中でベークしたものは約300N/m、大気中でベークしたものは約900N/mのピール強度が得られ、両者には大きな違いが認められた。このことは、ポリイミドとニッケル膜との界面にニッケルの酸化膜ができると密着性が向上することを示している。

【0058】(実施例7) 実施例4に記載した方法でポリベンゾオキサゾールフィルムを得た。このフィルムから5cm×5cmの試料片を3枚作り、これをドライエッチング装置(アネルバ社製、DEA-506)を用い、反応ガスとして窒素を用いてプラズマ処理を行った。処理条件は、出力800W、処理時間25分、圧力3Pa、流量25SCCMである。処理後、試料片をガラスクロス入りエポキシ樹脂基板に貼り付けた。その後、試料片に、各々チタン、コバルト、スズ、ニッケルを約1μmほどスパッタした。次に、試料をエポキシ樹脂基板からはがし、酸素気流下に1時間置いた。これらの試料のポリベンゾオキサゾールフィルム側から低角でX線を照射して回折スペクトルを測定してポリベンゾオキサゾールフィルムと金属膜との界面の状態を調べ、いずれの金属試料の場合にも界面に酸化膜が存在していることを確かめた。その後、各スパッタ金属膜上に実施例1と同じ条件で電気銅めつきで銅を膜厚約20μmほど厚づけた。電気銅めつき後、25℃のもと3時間真空乾燥を行った。銅膜を両面テープにてシリコンウエハに固定し、ポリベンゾオキサゾールフィルム側を引き剥がすピールテストを行った。ピールテスト時の剥離界面は、いずれの試料の場合にも、ポリベンゾオキサゾールと各種金属膜の界面で剥離していた。チタン、コバルト、スズ、ニッケルの各試料のピール強度は、各々0.6、0.8、0.8、1.0kN/mと高い密着力が得られた。また、これらの基板試料を窒素雰囲気中300℃で1時間放置した後のピール強度はほとんど変化していなかった。さらに、この基板試料を150℃の大気中で1000時間保持した後、ピール試験を行ったところピール強度はいずれの場合にも0.5kN/mと高い密着強度を保っていた。このことは、これらの基板を電子部品として使用した場合に熱的安定性において信頼性が高いことを示している。

【0059】(実施例8) 実施例4に記載した方法でポリベンゾオキサゾールフィルムを得た。このフィルムから10cm×10cmの試料片を作り、これをドライエッチング装置(アネルバ社製、DEA-506)を用い、反応ガスとして、アルゴン、酸素及び窒素を用いてプラズマ処理を行った。処理条件は、出力800W、処理時間25分、圧力3Pa、流量25SCCMである。

【0060】試料片をエポキシ樹脂基板に貼り付け、日本鉱業社製サーキットブレッダー3040、3340及び4041を用いて所定の方法でめつき用触媒処理を行った。次に、無電解ニッケルめつき(奥野製薬社製トッ

ブケミアロイB-1)を行い、ニッケルを膜厚1.0 μm つけた。試料をエポキシ樹脂基板からはがし、40℃に加熱しながら3時間真空乾燥した後、酸素気流下に1時間置いた。試料の樹脂フィルム側から低角でX線を照射して回折スペクトルを測定し、樹脂フィルムとニッケル膜との界面の状態を調べたところ、界面にニッケル酸化物が存在していることが分かった。その後、実施例1と同じ条件で電気銅めっきで銅を膜厚約20 μm ほど厚づけした。次に、樹脂フィルム側を両面テープにてシリコンウエハに固定し、銅膜を引き剥がすピールテストを行った。その結果、ピール強度は、反応ガスがアルゴン、酸素及び窒素の場合、それぞれ0.6、0.9、1.0 kN/m と高い密着力が得られた。また、これらの基板試料を窒素雰囲気中300℃で1時間放置した後のピール強度はほとんど変化していなかった。さらに、この基板試料を150℃の大気中で1000時間保持した後、ピール試験を行ったところピール強度はいずれの場合にも約0.5 kN/m と高い密着強度を保っていた。このことは、これらの基板を電子部品として使用した場合に熱的安定性において信頼性が高いことを示している。

【0061】(実施例9)樹脂基板として宇部興産社製ユーピレックス12.5Sを用いた。このフィルムから10cm×10cmの試料片を3枚作り、これらをドライエッチング装置(アネルバ社製、DEA-506)を用い、反応ガスとして、各々アルゴン、酸素及び窒素を用いてプラズマ処理を行った。処理条件は、出力800W、処理時間25分、圧力3Pa、流量25SCCMである。

【0062】試料片をエポキシ樹脂基板に貼り付け、日本鉱業社製サーキットブレッダー3040、3340及び4041を用いて所定の方法でめっき用触媒処理を行った。次に、無電解ニッケルめっき(奥野製薬社製トッブケミアロイB-1を使用)を行い、ニッケルを膜厚1.0 μm つけた。試料をエポキシ樹脂基板からはがし、40℃に加熱しながら3時間真空乾燥した後、酸素気流下に1時間置いた。試料の樹脂基板側から低角でX線を照射して回折スペクトルを測定し、樹脂基板とニッケル膜との界面の状態を調べたところ、界面にニッケル酸化物が存在していることが分かった。その後、実施例1と同じ条件で電気銅めっきで銅を膜厚約20 μm ほど厚づけした。次に、銅膜を両面テープにてシリコンウエハに

固定し、樹脂フィルム側を引き剥がすピールテストを行った。その結果、ピール強度は、反応ガスがアルゴン、酸素及び窒素の場合、それぞれ0.8、1.0、1.2 kN/m と高い密着力が得られた。また、これらの基板試料を窒素雰囲気中300℃で1時間放置した後のピール強度はほとんど変化していなかった。さらに、この基板試料を150℃の大気中で1000時間保持した後、ピール試験を行ったところピール強度はいずれの場合にも約0.6 kN/m と高い密着強度を保っていた。このことは、これらの基板を電子部品として使用した場合に熱的安定性において信頼性が高いことを示している。

【0063】(実施例10)ポリイミドの原料となるアミンとしてp-フェニレンジアミン(PDA)、4,4'-ジアミノジフェニルエーテル(DDE)を選び、酸無水物としてピロメリット酸二無水物(PMDA)、3,3',4,4'-ベンゾフェノンテトラカルボン酸二無水物(BTDA)、3,3',4,4'-ビフェニルテトラカルボン酸二無水物(BPDA)を選び、両者を等モルずつN-メチルピロリドンに溶かし室温付近で約5時間反応させてポリイミドの前駆体であるポリアミック酸を合成した。その後、10 μm のメンブランフィルタを用いて加圧濾過を行い、微小な不溶成分を除去した。このポリアミック酸ワニスガラス基板上にスピンコート法により塗布し、100℃で1時間加熱した後ガラス基板から剥がしてフィルムを得た。次に、このフィルムを鉄棒で固定した後窒素ガス雰囲気下で100℃から400℃まで90分で連続昇温し、イミド化反応を行わせてポリイミドフィルムを得た。このフィルムを10mm角にきり、試料とした。

【0064】エッチング速度は、この試料片を30℃に調節したヒドラジンヒドラート/エチレンジアミン(重量比7:3)の混合液約10cc入った試験管に所定の時間浸漬後、ポリイミドの膜厚減少をタリステップ(RANK TAILOR HOBSON社製)で測定して求めた。ただし、エッチングによりポリイミドは膨潤するため、水洗後200℃で乾燥した後膜厚を測定した。結果を表1に示す。市販されているポリイミドフィルムのKapton 200H(東レデュボン社製)とUpilex-25S(宇部興産社製)の評価結果も合わせて示した。

【0065】

【表1】

表 1

	ポリイミド		エッチング速度 ($\mu\text{m}/\text{分}$)	無電解めっき中の剥離 ○：剥離無し ×：剥離あり
	アミン	酸無水物		
合成 品	PDA	PMDA	10.3	×
	PDA	BTDA	0.3	○
	PDA	BPDA	0.04	○
	DDE	PMDA	1.5	×
	DDE	BTDA	0.06	○
	DDE	BPDA	0.03	○
市販 フィ ルム	Kapton 200H		10.1	×
	Upilex 25S		0.03	○

【0066】また、 $10\text{cm} \times 10\text{cm}$ の試料片を作り、これをドライエッチング装置（アネルバ社製、DEA-506）を用いて酸素プラズマ処理を行った。処理条件は、出力800W、処理時間25分、圧力3Pa、流量25SCCMである。処理後、試料片をガラスクロス入りエポキシ樹脂基板に貼り付け、日本鉱業社製サーキットブレッダー3040、3340及び4041を用いて所定の方法でめっき用触媒処理を行った。つぎに、無電解ニッケルめっき液（奥野製薬社製B-1）でニッケルを膜厚約 $1\mu\text{m}$ ほどつけた。めっき後、試料を酸素気流*

〔厚付け用無電解銅めっき液組成〕

・硫酸銅5水和物	0.04モル/l
・エチレンジアミン四酢酸二ナトリウム	0.1モル/l
・ホルムアルデヒド	0.03モル/l
・水酸化ナトリウム	0.1モル/l
・2, 2'-ビピリジル	0.0002モル/l
・ポリエチレングリコール(平均分子量6000)	0.03モル/l

めっき中めっき膜の剥離が起きたかどうかを観察した。その結果を表1に示す。エッチング速度の遅いポリイミドフィルムを基板に用いたときには剥離が観測されなかったが、エッチングされやすいポリイミドの場合には、めっき開始30分ほどでポリイミドとニッケル膜との間で剥離が起きた。表1の結果は、基板のポリイミドの耐アルカリ性の強弱が無電解銅めっき中の剥離の有無に大きく影響していることを示し、エッチング速度が $1\mu\text{m}/\text{分}$ 以下であると無電解銅めっき中の剥離を防ぐことができることがわかる。

【0068】（実施例11）実施例10に記載した方法で作製したポリイミドフィルムを $5\text{cm} \times 5\text{cm}$ 角とし、それぞれの種類のポリイミドごと2枚ずつ用意した。各種類1枚ずつを実施例10に記載の条件で酸素プラズマ処理を行った後、試料片をガラスエポキシ樹脂基板に貼り付け、処理面に銅をスパッタリングで膜厚約 $1\mu\text{m}$ ほどつけた。未処理のフィルムについても銅をスパッタリングで膜厚約 $1\mu\text{m}$ ほどつけた。すべての試料を酸素気流下に1時間ほどおいた。試料のポリイミド側から低角でX線を照射して回折スペクトルを測定し、ポリイミドと

*下に1時間ほどおいた。試料の樹脂基板側から低角でX線を照射して回折スペクトルを測定し、樹脂基板とニッケル膜との界面の状態を調べたところ、界面にニッケル酸化物が存在していることが分かった。後、塩化パラジウム水溶液（ $1\text{g}/\text{l}$ ）に1分ほどつけた後厚付け用無電解銅めっき浴に入れ銅めっきを行った。厚付け用無電解銅めっき液の組成は以下の通りである。液温は 70°C に保持した。

【0067】

銅膜との界面の状態を調べたところ、界面に銅酸化物が存在していることが分かった。これらの試料のポリイミドフィルム側から低角でX線を照射して回折スペクトルを測定し、ポリイミドフィルムと金属膜との界面の状態を調べたところ、いずれの試料の場合にも、界面に銅の酸化物が存在していることが分かった。その後、すべての試料について電気銅めっきで銅を膜厚約 $20\mu\text{m}$ ほど厚付けした。用いた電気銅めっき液の組成は実施例1と同じである。電流密度は $0.015\text{A}/\text{cm}^2$ とした。銅膜を両面テープにてシリコンウエハに固定し、 25°C のもと、ポリイミドフィルムの銅がついていない側を 90° の角度で上方に引き上げて引き剥がすピールテストを行った。その結果を表2に示す。市販されているポリイミドフィルムのKapton 200H（東レデュボン社製）とUpilex-25S（宇部興産社製）の評価結果も合わせて示した。いずれのポリイミドの場合にも、酸素プラズマ処理を施すと未処理の場合に比べ密着力が著しく向上した。

【0069】

〔表2〕

表 2

	ポリイミド		ピール強度 (N/m)	
	アミン	酸無水物	未処理	酸素プラズマ処理
合 成 品	PDA	PMDA	50	600
	PDA	BTDA	100	900
	PDA	BPDA	50	600
	DDE	PMDA	150	1300
	DDE	BTDA	80	800
	DDE	BPDA	<30	700
市販 フィ ルム	Kapton 200H		50	600
	Upilex 25S		<30	700

【0070】（実施例12）p-フェニレンジアミン（PDA）と3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物（BPDA）の組み合わせからなるポリイミドのフィルムを実施例10に記載した方法により得た。試料フィルムは5cm×5cm角とし、4枚用意した。このフィルムを実施例10に記載した条件で酸素プラズマ処理を行った。その後、試料片をガラスエポキシ樹脂基板に貼り付け、実施例1に記載したものと同様な方法でめっき用の触媒処理を行った。これらの試料フィルムにそれぞれ無電解ニッケルめっき（奥野製薬社製トップケミアロイB-1使用、膜厚約1.0μm）、無電解コバルトめっき（奥野製薬社製ディスクラッド601使用、膜厚約0.8μm）、無電解銅めっき（奥野製薬社製サブスターSN-2使用、膜厚約0.7μm）及び薄付け用無電解銅めっき（日立化成社製CUST-2000使用、膜厚約0.3μm）を行った。めっき後、試料を電気炉で180℃のもと2時間ベークした。試料のポリイミドフィルム側から低角でX線を照射して回折スペクトルを測定し、ポリイミドと金属膜との界面の状態を調べたところ、界面に各種金属の酸化物が存在していることを確かめた。そのあと、薄付け用銅めっきをした試料はそのまま、銅以外の金属をめっきした試料の場合には塩化パラジウム水溶液（1g/l）に30秒ほどつけた後厚付け用無電解銅めっき浴に入れ銅めっきを行った。厚付け用無電解銅めっき液の組成は実施例10と同様で、液温は70℃に保持した。めっき開始後凡そ20秒ほどで薄付け用銅めっきをした試料では、めっき膜の剥離が観測された。それに対し、銅以外の金属をめっきした試料では3時間ほど経過しても剥離は観測されなかった。薄付け用銅めっきをした試料では、ポリイミドとの界面できている酸化銅膜が、厚付け用無電解銅めっき中に還元されるため剥離が起きたものと推測される。銅の還元電位よりも還元電位が卑である金属で、表面処理を施した樹脂基板表面を覆ってから厚付け用無電解銅めっきを行うと酸化物の還元反応が起きず、ポリイミドと金属の界面が破壊されずにすむために剥離が起きなくなるものと考えられる。したがって、厚付け用無電解銅めっき

を行う前に、還元電位が卑である金属で樹脂基板表面を覆うことは、不可欠であるといえる。

【0071】（実施例13）ポリイミドフィルムからなる樹脂基板として宇部興産社製ユービレックス25Sを用いた。10cm×10cmの試料片を作り、これをドライエッチング装置（アネルバ社製、DEA-506）を用いて酸素プラズマ処理を行った。処理条件は、圧力3Pa、流量25SCCMである。プラズマの出力は200-800W、処理時間は5-45分の間で変化させた。また、反応ガスとして窒素を用い、同じ処理条件でプラズマ処理を行った。これらの処理を行った処理面を表面形態解析装置（エリオニクス社製ESA-3000）で観察し中心線平均粗さ（Ra）を求めた。また、処理した試料片をガラスエポキシ樹脂基板に貼り付け、実施例10に記載したと同様な処理方法でめっき用触媒処理を行った。つぎに、無電解ニッケルめっき液（奥野製薬社製B-1）でニッケルを膜厚約1μmほどつけた。試料を大気中電気炉で180℃のもと2時間ベークした。試料の樹脂基板側から低角でX線を照射して回折スペクトルを測定し、樹脂基板とニッケル膜との界面の状態を調べたところ、界面にニッケル酸化物が存在していることが分かった。その後、塩化パラジウム水溶液（1g/l）に30秒ほどつけ、その後実施例10に記載した厚付け用無電解銅めっき浴に入れ銅めっきを行い、銅を膜厚約20μmほど厚づけした。液温は70℃に保持した。その後、銅膜がついている側を両面テープにてシリコンウエハに固定し、25℃のもと、ポリイミドフィルムを90度上方に引き上げるピール試験を行った。その結果を中心線平均粗さ（Ra）の測定値とともに表3に示す。酸素プラズマ処理の場合にも、窒素プラズマ処理の場合にも、Raが0.1μm以上の場合に高いピール強度が得られることが分かる。一方、プラズマ処理時間が長く、Raが1.0μm以上になると、逆にピール強度が減少している。剥離界面を観測すると、剥離したニッケル膜側に樹脂成分が付着していたことから、プラズマ処理によってポリイミド表面が脆くなってしまい、そのためピール強度が減少したものと考えられる。したが

って、Raが0.1 μ m以上かつ1.0 μ m以下になるようにプラズマ処理することが適当である。これによって、0.5kN/m以上の高い密着力を示す銅の配線基*

表 3

反応ガス	出力(W)	処理時間(分)	Ra(μ m)	ピール強度(N/m)
酸素	400	15	0.05	400
	800	5	0.07	500
	800	15	0.13	700
	800	25	0.19	900
	800	50	0.75	800
	800	75	1.32	300
窒素	400	15	0.06	400
	800	5	0.11	600
	800	15	0.15	1100
	800	25	0.21	1300
	800	50	0.53	1100
	800	75	1.05	400

【0073】(実施例14) ポリイミドフィルムからなる樹脂基板として宇部興産社製ユービレックス50Sを用いた。10cm×10cmの試料片を2枚作り、これらにドライエッチング装置(アネルバ社製、DEA-506)を用いて窒素プラズマ処理を行った。処理条件は、出力800W、処理時間25分、圧力3Pa、流量25SCCMである。処理表面の中心線平均粗さ(Ra)を実施例13と同様に測定したところ、0.2 μ mであった。処理後、試料片をガラスエポキシ樹脂基板に貼り付け、実施例10に記載したと同様な処理方法でめっき用触媒処理を行った。つぎに、各々の試料に、無電解コバルトめっき(奥野製薬社製ディスクラッド601使用、膜厚約0.8 μ m)、無電解銅めっき(奥野製薬社製サブスターSN-2使用、膜厚約0.7 μ m)を行った。めっき後、試料を大気中電気炉で180℃のもと2時間ベークした。その後、塩化パラジウム水溶液(1g/l)に30秒ほどつけ、その後実施例10に記載した厚付け用無電解銅めっき浴に入れ銅めっきを行った。液温は70℃に保持した。めっきを10時間ほど行っても剥離は観測されず、膜厚約20 μ mほど銅をめっきできた。めっき後に、25℃のもとポリイミドフィルムを90度上方に引き上げて引き剥がすピールテストで銅膜との密着力を評価したところ、ピール強度は、コバルト及び銅をめっきした試料の場合各々約900、約800N/mであり、無電解銅めっきにより十分な密着力を持った銅の厚膜をポリイミドフィルム上に形成できた。また、これらの基板試料を窒素雰囲気中で300℃の高温下に2時間おいた後のピール強度を測定したところ、ピール強度は加熱処理前と同等な高いピール強度を示し、加熱処理によっても密着性が低下せず、耐熱性に対して高い信頼性を持つ配線基板を製造できた。

* 板を無電解銅めっきにより製造できる。

【0072】

【表3】

【0074】(実施例15) ポリイミドフィルムからなる樹脂基板として宇部興産社製ユービレックス50Sを用いた。10cm×10cmの試料片を作り、これをステンレス板に貼り付け固定し、実施例10に記載した条件で酸素プラズマ処理を行った。処理後、実施例10に記載した方法によりめっき用触媒を付与した。次に、試料片表面に感光性ネガ型ドライフィルムをラミネートし、露光現像してめっきレジストを形成した。最小のレジストのライン/スペース間隔は20 μ mであった。試料片をステンレス板から剥がし、無電解ニッケルめっき液(奥野製薬社製B-1)でニッケルを膜厚約1 μ mほどつけた。試料を大気中電気炉で180℃のもと2時間ベークした後、塩化パラジウム水溶液(1g/l)に30秒ほどつけ、その後実施例10に記載した厚付け用無電解銅めっき浴に入れ銅めっきを行った。液温は70℃に保持した。めっきを10時間ほど行ってもレジスト、めっき銅膜とも剥離は起きず、膜厚約20 μ mほど銅をめっきできた。銅配線部分とポリイミド基板との間で剥離ではなく、良好な密着性を示した。銅配線部分を光学顕微鏡及び走査型電子顕微鏡で観察したところ、レジストの形状を良く再現した銅配線パターンが得られていた。ライン/スペース間隔20 μ mの銅配線パターンが形成できることが確認された。銅配線部の断面を観察すると、ニッケルと銅の界面にはわずかな段差も見られず、銅配線部の形状は、レジストの形状のレプリカとして忠実に再現されていた。また、ライン幅5mmの配線を90度上方へ引き剥がすピール試験を行ったところ、ピール強度は約900N/mと非常に高い値が得られた。さらに、この基板試料を窒素雰囲気中で300℃の高温下に2時間おいた後のピール強度を測定したところ、ピール強度は約900N/mと加熱処理前と同等な高いピール強度を

示し、加熱処理によっても密着性が低下せず、耐熱性に対して高い信頼性を持つ配線基板を製造できた。

【0075】(実施例16) 実施例4に記載した方法でポリベンゾオキサゾールフィルムを得た。膜厚は40 μ mであった。このフィルムを10mm角に切り、試料とした。実施例10に記載した方法と同じ方法でエッチング速度を測定したところ、エッチング速度は、約0.6 μ m/分であった。次に、10cm \times 10cmの試料片を作り、これを実施例10に記載した条件で酸素プラズマ処理を行った。処理後、試料片をガラスエポキシ樹脂基板に貼り付け、実施例10に記載したと同様な処理方法でめっき用触媒処理を行った。つぎに、無電解ニッケルめっき液(奥野製薬社製B-1)でニッケルを膜厚約1 μ mほどつけた。試料を大気中180 $^{\circ}$ Cのもと2時間ベークした後、塩化パラジウム水溶液(1g/l)に30秒ほどつけ、実施例10に記載した厚付け用無電解銅めっき浴に入れ銅めっきを行った。液温は70 $^{\circ}$ Cに保持した。めっきを10時間ほど行っても剥離は観測されず、膜厚約20 μ mほど銅をめっきできた。めっき後に、25 $^{\circ}$ Cのもと、銅膜を90度上方に引き上げて引き剥がすピールテストで銅膜との密着力を評価したところ、ピール強度は約700N/mであり、十分な密着性が得られた。また、この試料を窒素雰囲気中300 $^{\circ}$ Cの高温下に2時間おいた後のピール強度を測定したところ、ピール強度は約650N/mと加熱処理前と同等なピール強度を示した。

【0076】(実施例17) ポリイミドフィルムからなる樹脂基板として宇部興産社製ユービレックス50Sを用いた。10cm \times 10cmの試料片を作り、これを実施例1に記載した表面改質処理水溶液で液温70 $^{\circ}$ Cのもとで処理を行った。処理後、試料片をガラスクロス入りエポキシ樹脂基板に貼り付け、実施例1に記載したと同様な処理方法でめっき用触媒処理を行った。つぎに、無電解ニッケルめっき液(奥野製薬社製B-1)でニッケルを膜厚約1 μ mほどつけた。試料を大気中電気炉で120 $^{\circ}$ Cのもと2時間ベークした。その後、塩化パラジウム水溶液(1g/l)に30秒ほどつけ、その後実施例10に記載した厚付け用無電解銅めっき浴に入れ銅めっきを行った。液温は70 $^{\circ}$ Cに保持した。めっきを10時間ほど行っても剥離は観測されず、膜厚約20 μ mほど銅をめっきできた。めっき後に、銅膜をウエハに固定しポリイミドフィルムを90度上方に引き上げて引き剥がすピールテストで銅膜との密着力を評価したところ、ピール強度は約900N/mであり、無電解銅めっきにより十分な密着力を持った銅の厚膜をポリイミドフィルム上に形成できた。したがって、すべての工程をウエットで行える低コスト化に有利な配線基板の製造方法を提供できる。

【0077】(実施例18) 銅張り積層板を用いてサブトラクト法で形成した導体回路層上に、フルアディティブ法で形成した微細配線層を積層した配線基板の製造方

法について説明する。製造プロセスを図6に示す。ポリイミドからなる樹脂板22に銅21張り積層板に感光性ドライフィルム(デュボン社製、リストン1051)をラミネートし、所望の導体回路パターンが描画されたマスクを通して紫外線露光させ画像を焼き付けた(a)。ついで1-1-1トリクロロエタンで現像を行い、塩化第二銅エッチング液を用いて非導体部の銅を除去した後、塩化メチレンでドライフィルムを剥離した(b)。この第一層導体回路の上に、(3-アミノプロピル)トリエトキシシラン(アルドリッチ社製)の20mMのトルエン溶液を浸漬塗工した後、110 $^{\circ}$ Cで30分乾燥した。その上にポリイミドワニス(日立化成社製PIQ-L100)を塗布し、硬化温度400 $^{\circ}$ Cでキュアし、膜厚約15 μ mのポリイミド層を得た。このポリイミド層表面の所定の位置に層間接続穴(ϕ 50 μ m)をエキシマーレーザ(KrF)により開口し、残さをデスミア処理で取り除いた(c)。次いで、表面層のポリイミド表面に、実施例10に記載した条件で酸素プラズマ処理、触媒付与を順次行った。次に、ポリイミド表面に感光性ネガ型ドライフィルムからなるレジスト24をラミネートし、マスクを通して露光し、現像してめっきレジストを形成した。めっきレジストを形成する際には、前工程で設けた接続穴、及びそのランドが露出するようにマスクを作製し、用いた。最小のレジストのライン/スペース間隔は20 μ mであった。次に、無電解ニッケルめっき液(奥野製薬社製B-1)でニッケル25を膜厚約1 μ mほどつけた。基板を大気中電気炉で180 $^{\circ}$ Cのもと2時間ベークした後、塩化パラジウム水溶液(1g/l)に10秒ほどつけ、その後実施例10に記載した厚付け用無電解銅めっき浴に入れ銅めっきを行い、ポリイミド層上の第二層導体回路パターンの形成と、第一層導体回路と第二層導体回路を接続する接続穴内の接続導体部の形成を行った。めっき浴の温度は70 $^{\circ}$ Cに保持し、めっきを8時間行い、膜厚約16 μ mの銅膜を形成した(d)。その後、接続穴を銅ペーストにより充填した。次に、再度ポリイミドワニスを塗布してポリイミド層を形成し、レーザで接続穴を開いた後感光性ドライフィルムをラミネート後、露光現像してめっき用レジストを設け、上記と同様に無電解めっきにより配線層形成、接続穴内部のメタライズを行い、最後に銅ペースト26を接続穴内に充填した(e)。作製した配線基板の斜視図を図7に示す。最上層の銅配線部分を光学顕微鏡及び走査型電子顕微鏡で観察したところ、レジストの形状を良く再現した銅配線パターンが得られており、ライン幅30 μ m、ライン/スペース間隔20 μ mの銅配線パターンが形成できていることが確認された。この基板を150 $^{\circ}$ Cの大気中に1000時間放置しても、断線、配線の剥離は観測されなかった。したがって、この配線基板は、長期にわたる高温下での動作に対する信頼性が高いものである。

【0078】(実施例19)シリコンウエハ基板上に、フルアディティブ法で形成した微細配線層を2層積層した配線基板の製造方法について説明する。製造プロセスの模式図を図8に示す。シリコンウエハに、(3-アミノプロピル)トリエトキシシラン(アルドリッチ社製)の20mMのトルエン溶液を浸漬塗工した後、110℃で30分乾燥した。その上にポリイミドワニス(日立化成社製PIQ-L100)を塗布し、硬化温度400℃でキュアし、ポリイミドフィルム32を得た(a)。膜厚は、5μmであった。このポリイミドフィルム表面に、実施例5に記載した条件で酸素プラズマ処理、触媒付与を行った。次に、試料表面に感光性ネガ型ドライフィルムをラミネートし、露光現像してめっきレジストを形成した。最小のレジストのライン/スペース間隔は20μmであった。次に、無電解ニッケルめっき液(奥野製薬社製B-1)でニッケル34を膜厚約0.4μmほどつけた。試料を大気中電気炉で180℃のもと2時間ベークした後、塩化パラジウム水溶液(0.2g/l)に10秒ほどつけ、その後実施例10に記載した厚付け用無電解銅めっき浴に入れ銅めっきを行った。液温は70℃に保持した。めっきを2.5時間ほど行ってもレジスト、めっき銅膜とも剥離は起きず、膜厚約5μmほど銅膜33をめっきできた。その後、めっきレジストを剥離した(b)。銅配線部分とポリイミドフィルムとの間で剥離などはなく、良好な密着性を示した。さらに、この第一配線層の上に、ポリイミドフィルム(宇部興産社製ユービレックス12.5S)を接着フィルム36(日立化成工業社製N4、接着温度250℃、膜厚10μm)を介して加熱プレスして接着し第二絶縁層を形成した(c)。この第二絶縁層表面の所定の位置に層間接続穴(φ50μm)をエキシマーレーザ(KrF)により開口し、残さをデスミア処理で取り除いた(d)。次いで、めっきレジスト37を用いて第一配線層を形成した場合と同様な工程を繰り返すことで、第二絶縁層上の第二層導体回路パターンの形成と、第一層導体回路と第二層導体回路を接続する接続穴内の接続導体部の形成を行った(e)。作製した基板をダイサで切断した後、断面を研磨し光学顕微鏡及び走査型電子顕微鏡で観察したところ、レジストの形状を良く再現した銅配線パターンが得られており、第一導体回路層と第二導体回路層ともに、ライン/スペース間隔20μmの銅配線回路パターンが形成できていること、層間接続穴においても穴の内側の銅めっきの付き回りが良く電氣的接続が確実にとれていることが確認された。また、この基板を150℃の大気中に1000時間放置しても、断線、配線の剥離は観測されず、この配線基板は長期にわたる高温下での動作に対する信頼性が高いものである。

【0079】(実施例20)常法の厚膜プロセスにより製造したセラミック基板上に、絶縁樹脂基板上にフルアディティブ法で銅配線を設けた配線基板を積層すること

により形成するマルチチップモジュール基板の製造方法について説明する。図9は、このモジュールの作製工程の実施例を説明する。ポリイミドフィルム(宇部興産社製ユービレックス12.5S)の片面にのみ実施例18と同様な方法で銅配線を形成し、片面に配線層を有した片面配線シート41を作製した。セラミック基板上にこの配線シートを接着フィルム42(日立化成工業社製N4、接着温度250℃、膜厚10μm)を介して、銅配線層側が接着フィルムと接する向きに、平行平板プレスを用いて接着した。その後、セラミック基板43上のパッド部と配線層との電氣的な接続をとるために所定の位置に層間接続穴(φ50μm)をエキシマーレーザ(KrF, 248nm)により開口し、残さをデスミア処理で取り除いた後、接続穴内を選択銅めっき法で膜厚5μmほどメタライズしたあと銅ペースト44を充填した(b)。

【0080】図10は、図9で得たセラミック基板上に6層の多層配線樹脂基板を設け、LSIチップをフリップチップボンディング法により搭載したマルチチップモジュールの部分断面図である。

【0081】この配線シートの上に、ポリイミドフィルムの両面に実施例18と同様な方法で銅配線を形成した配線シートを、前記と同様の接着フィルム42を介して平行平板プレスを用いて接着した。次に、ポリイミドフィルム(宇部興産社製ユービレックス12.5S)の片面にのみ実施例18と同様な方法で銅配線を形成して作製した片面配線シート41を、前記と同様の接着フィルム42を介して、銅配線層側が接着フィルムと接する向きに、平行平板プレスを用いて接着した。積層したシートの表面の所定の箇所をエキシマーレーザ(KrF, 248nm)により開口し、表面層(Cr/Ni/Au)を形成した。その後、フリップチップボンディングでLSIチップを複数個を搭載し、マルチチップモジュールを作製した。この配線基板は、半田接続プロセスを経ても断線、配線の剥離は観測されず、高温プロセスに対する信頼性が高いことが分かった。

【0082】

【発明の効果】本発明によれば、導体金属と樹脂基板との密着性に優れ、かつ耐熱性に優れた信頼性の高い配線基板を得ることができる。その結果、所望の厚さを有し、ライン幅として40μm以下の微細配線が可能となる。

【0083】また、上記の配線基板を複数積層することにより積層基板とし、各層間の電氣的な接続を行い、最表面にICとの接続部を設けてICを搭載することで、耐熱性に優れた信頼性の高いマルチチップモジュールを得ることができる。

【図面の簡単な説明】

【図1】本発明の配線基板の構成を示す断面図である。

【図2】カプトン200Hの処理前後の全反射赤外吸収

スペクトルを示す図である。

【図3】カプトン200Hの処理前後の全反射赤外吸収の差スペクトルを示す図である。

【図4】表面処理を施したカプトン200Hのめっき前後の全反射赤外吸収の差スペクトルの変化を示す図である。

【図5】表面処理を施したカプトン200Hに銅を電気めっきした後のピール強度の経時変化を示す図である。

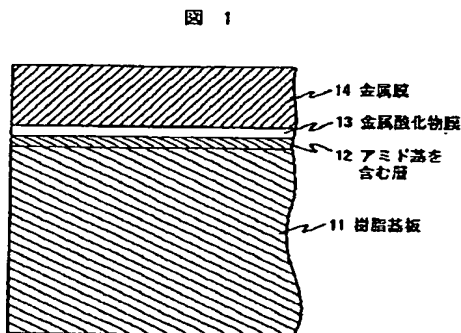
【図6】銅張り積層板を用いた配線基板の製造工程を模式的に示した工程図である。

【図7】銅張り積層板を用いて製造した配線基板の斜視図である。

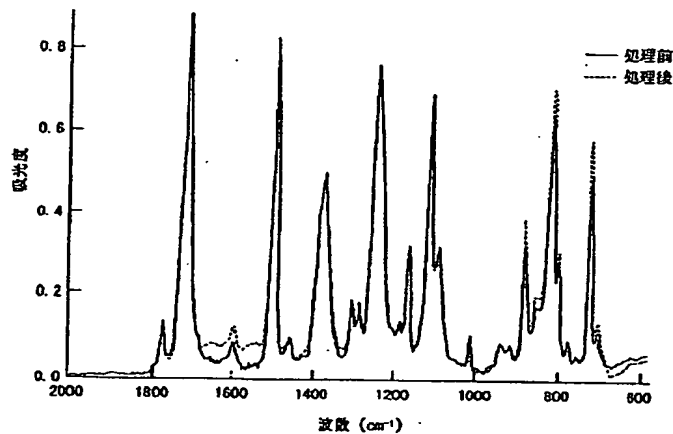
【図8】シリコンウエハ基板上にフルアディティブ法で2層積層した配線基板の製造プロセスを模式的に示した工程図である。

【図9】セラミック基板上に樹脂フィルム配線層を形成*

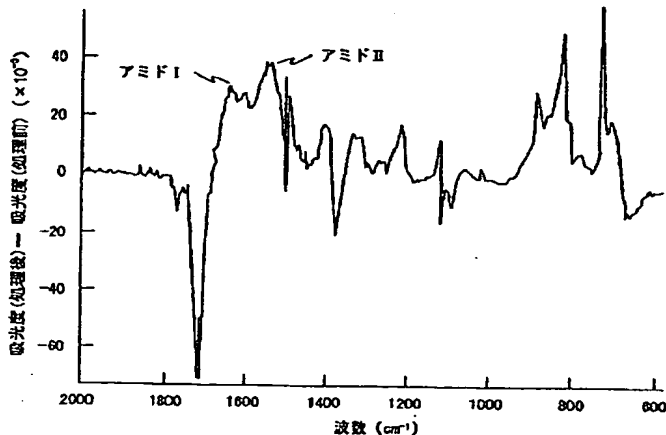
【図1】



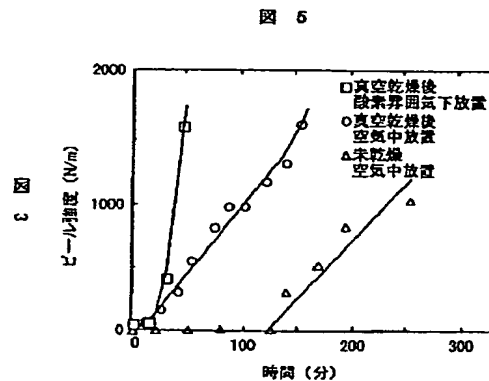
【図2】



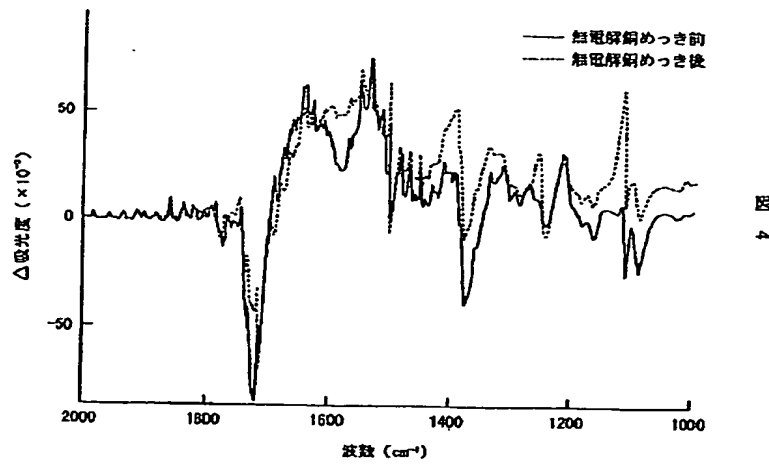
【図3】



【図5】

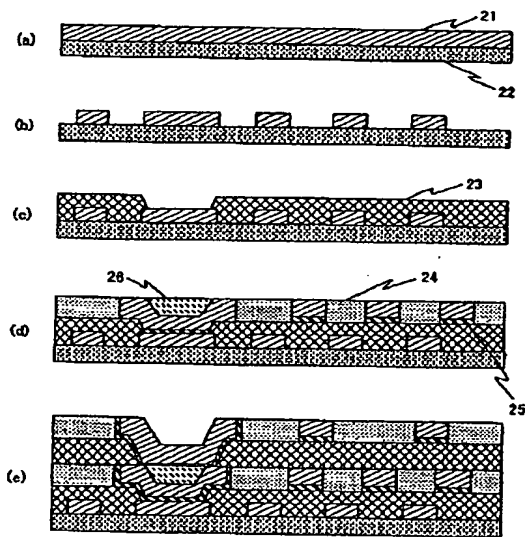


【図4】



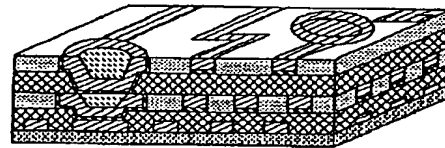
【図6】

図 6



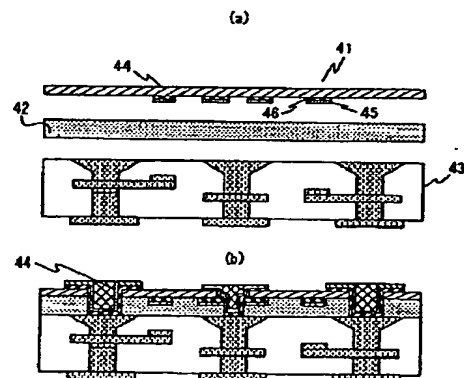
【図7】

図 7

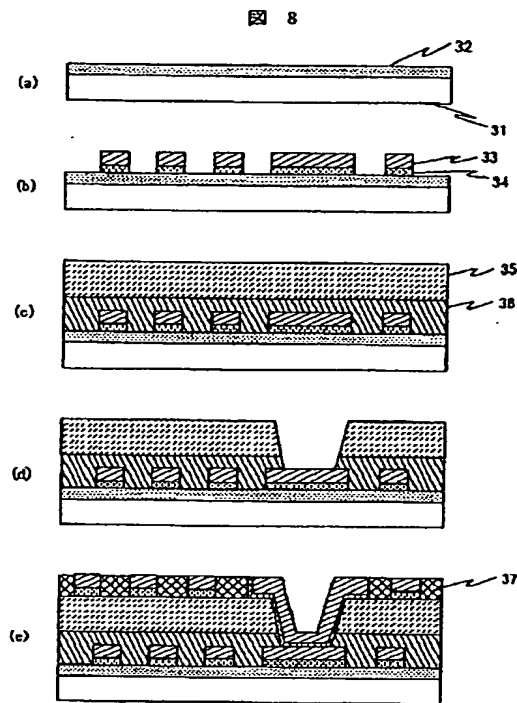


【図9】

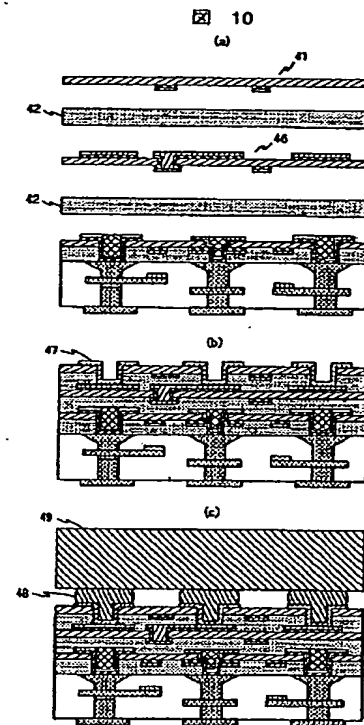
図 9



【図8】



【図10】



フロントページの続き

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Fターム(参考) 5E343 AA12 AA38 BB24 BB34 BB44
BB45 BB52 BB59 DD33 EE46
GG01
5E346 BB15 CC08 CC10 CC32 CC33
CC37 CC40 DD23 DD33 HH31